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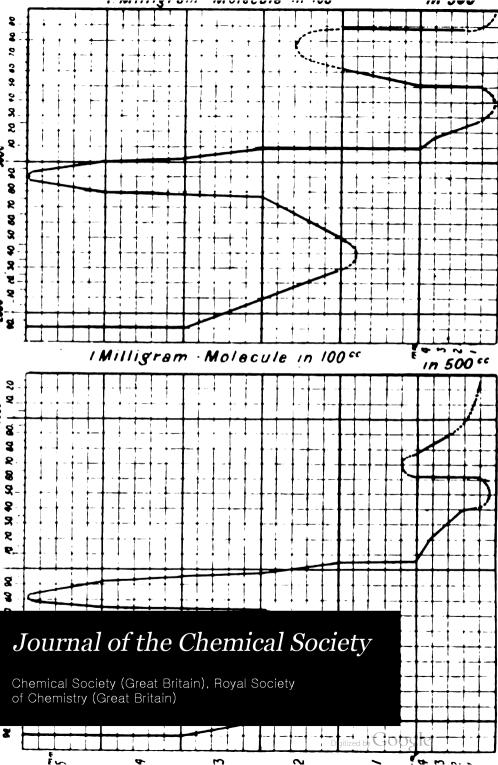
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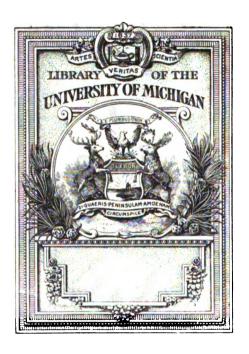
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OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—The Oxidation of Polyhydric Alcohols in Presence of Iron.

By Henry J. Horstman Fenton, M.A., and Henry Jackson, B.A., B.Sc.

THE specific influence which ferrous iron exerts on the oxidation of certain hydroxy-acids has been pointed out by one of the authors in several previous communications (Trans., 1894, 65, 899; Proc., 1898, &c.). In the case of tartaric acid, for example, two atoms of hydrogen are removed from a molecule of the acid with the production of dihydroxymaleic acid. For the purpose of bringing about this change, the presence of ferrous iron is absolutely essential, but its proportion bears little, if any, relation to the yield of the product, the influence of the iron being apparently of the nature usually described as 'catalytic.' The most efficient oxidising agent for the purpose is found to be hydrogen dioxide, but a similar result may be obtained by chlorine, potassium permanganate, &c., by electrolysis, and by atmospheric oxygen in presence of sunlight.

The study of this oxidation process is now being extended to several other hydroxy-acids, and Messrs. Morrell and Cross have undertaken its application to certain carbohydrates. Aiming at a complete investigation of the reaction as regards various typical classes of hydroxy-compounds, the present authors are making a series of observations on the behaviour of various alcohols, and this communication deals with the results which have so far been obtained. It will be shown that, in the case of all the polyhydric alcohols examined, the presence of ferrous iron exerts a remarkable influence

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on the oxidation by hydrogen dioxide, and that in its absence the results are practically nil.

In carrying out the experiments, a weighed quantity of the alcohol was dissolved in water, mixed with a solution of ferrous sulphate (corresponding to about \(\frac{1}{10} \) to \(\frac{1}{4} \) atom Fe * per molecule of alcohol employed) and strong ('20 volume') hydrogen dioxide, previously standardised by permanganate, was gradually added; in every case, a blank experiment was made with exactly similar proportions and under the same conditions, but omitting the iron. A blank experiment was also made, for comparison, with ferrous sulphate and hydrogen dioxide alone; 5 grams of crystallised ferrous sulphate being dissolved in 20 c.c. of water, and about 10 c.c. of the peroxide gradually added. The rise of temperature was very slight, and was quite insignificant in comparison with that obtained in the cases mentioned below; the liquid gave only a brown colour or precipitate with Fehling's solution in the cold, without any sign of reduction, and gave no indication with Schiff's rosaniline test.

Monhydric Alcohols.

Methylic, ethylic, propylic, isopropylic, and amylic alcohols were examined. The experiments were made by taking 10 grams of the alcohol, diluting with water, dividing the solution into two equal parts, to one of which 0.5 gram of crystallised ferrous sulphate, dissolved in a little water, was added, and each part was then mixed with the standardised hydrogen dioxide in the proportion of 1 mol. H₂O₂ to 1 mol. of the alcohol. No perceptible rise of temperature occurred in any case either in presence or absence of iron, and the solutions gave practically no indication with Fehling's solution or with Schiff's rosaniline test. The results were, in fact, entirely negative under the conditions of the experiments, at any rate, as regards the production of aldehydic substances, nor could acetone be detected in the case of isopropylic alcohol.

Ethylene Glycol.

On adding hydrogen dioxide to a strong aqueous solution of ethylene glycol, in presence of a ferrous salt, a very sensible rise of tem-

* In the case of tartaric acid, only $_{1\bar{1}0}$ atom Fe, or less, was employed for one molecule of acid, but in the present investigation it was found advisable to use a larger proportion, and possibly it may be advantageous still further to increase the quantity. The reason for this difference is probably to be found in the fact that, in the former case, the ferric salt formed is almost instantly reduced at the expense of a portion of the dihydroxymaleic acid (Proc., May, 1898, 119), a result which apparently is not produced by the oxidation products here mentioned.

perature occurs, and heat continues to be evolved for a considerable time after the solutions are mixed; the product almost immediately restores the colour to a rosaniline salt previously bleached by sulphur dioxide, and reduces Fehling's solution in the cold. Phenylhydrazine acetate, after a few minutes, gives a yellowish-brown, crystalline precipitate, which continues to separate at the ordinary temperature for some days. In an exactly parallel blank experiment, omitting the iron salt, there is no perceptible rise of temperature, and the solution does not reduce Fehling's solution in the cold; it gives, however, a faint indication with the rosaniline test, and phenylhydrazine acetate produces after a time a small amount of precipitate somewhat resembling in appearance that above mentioned, but more discoloured and resinous.

From these results, it would appear that, although glycol is very slightly oxidised by hydrogen dioxide alone, the action is insignificant in comparison with that produced in presence of iron.

In order to investigate the nature of the product of oxidation, 6.2 grams of ethylene glycol were dissolved in 70 c.c. of water, and mixed with a solution of 5.2 grams of crystallised ferrous sulphate: to the mixture was gradually added 65.6 c.c. of hydrogen dioxide containing 0.0559 H₂O₂ per c.c. The temperature began to rise immediately, and increased considerably after a few minutes. standing 11 hours, a solution of sodium acetate was added (to remove free mineral acid present in the peroxide), and the solution was then mixed with 21.5 grams of phenylhydrazine dissolved in 50 per cent. acetic acid. The mixture was heated in a regulated water bath at 38° for 5 hours, allowed to stand 12 hours at the ordinary temperature, and the precipitate was then filtered off, washed, and dried in the air; the weight of crude osazone thus obtained was 2.8 grams. A parallel experiment was made with a similar quantity of glycol, but omitting the ferrous salt, and using the same quantity of phenylhydrazine, &c., and heating exactly as before; the precipitate formed in this case weighed only 0.35 gram.

The crude osazone obtained in the above manner was first rubbed with a very little cold absolute alcohol, which removed a little resinous matter, and the undissolved yellow powder was twice recrystallised from hot absolute alcohol, from which it separated in yellow, transparent plates, melting sharply at 169.5°, and exactly resembling in every way the product previously obtained from glycollic aldehyde (Trans., 1895, 67, 774).

The substance, dried at 100°, gave the following results on analysis. 0-0900 substance gave 0.2326 CO₂ and 0.0480 $\rm H_2O$; C=70.49; H=5.92. $\rm C_{14}H_{14}N_4$ requires C=70.58; H=5.88 per cent.

The substance is, therefore, glyoxalosazone, $CH: N_2H \cdot C_6H_5$, and the oxidation product from which it was obtained may consequently be either glycollic aldehyde or glyoxal.

Another similar quantity of glycol was now oxidised in presence of iron as before, the mixture well shaken with pure chalk, filtered, and the filtrate evaporated to a syrup in a vacuum desiccator; absolute alcohol and a few drops of ether were then added, and the precipitated calcium salts filtered off. The solution, on again evaporating in a vacuum, left a syrup soluble in alcohol but nearly insoluble in ether, and showing all the reactions of glycollic aldehyde; it was partially volatile with steam, reduced Fehling's solution and ammoniacal silver nitrate in the cold, and immediately answered Schiff's rosaniline test.

On shaking a strong aqueous solution of this syrup with excess of freshly prepared sodium hydrogen sulphite, no crystalline substance was obtained even on allowing the mixture to stand for some days. It was thought that, on using twice the proportion of hydrogen dioxide (2 mols.), glyoxal might perhaps be formed, but on making another similar experiment with this proportion, no compound with the sulphite could be obtained. The result of the oxidation conducted in the above way is, therefore, glycollic aldehyde.

Glycerol.

When a solution of glycerol (1 mol.) is mixed gradually with strong (20 volume) hydrogen dioxide (1 mol.) at the ordinary temperature, little, if any, change takes place. No alteration of temperature occurs, and the mixture, even after some days, gives very strong reactions of hydrogen dioxide; Fehling's solution, in the cold, is not reduced, and the addition of phenylhydrazine acetate merely gives rise to an evolution of gas owing to the presence of hydrogen dioxide, and there is a slight precipitation of resinous matter. When, however, an exactly parallel experiment is made with the previous addition of a small quantity of ferrous sulphate in solution, a very powerful action results. The peroxide is now consumed almost immediately, and the temperature rises very considerably, in fact, if the peroxide is added quickly, and the solutions are strong, the vessel becomes almost too hot to be held in the hand. The solution, when cold, now strongly . reduces Fehling's solution in the cold, immediately answers Schiff's rosaniline test, and if it is mixed with phenylhydrazine acetate, a bulky, yellowish-brown, crystalline precipitate begins to separate at the ordinary temperature, and continues to do so for several days.

If a ferric salt be substituted for ferrous in the above experiment, the result is entirely negative. In order to investigate the nature of

the product, 10 grams of glycerol, diluted with an equal bulk of water, was mixed with a solution of 1 gram of crystallised ferrous sulphate, and 45 c.c. of hydrogen dioxide (of the before-mentioned strength) was slowly added, the rise of temperature being moderated by immersing the vessel in cold water. Sodium acetate and 20 grams of phenylhydrazine, as acetate, were then added as before, and the mixture was left for some days at the ordinary temperature; the precipitate formed was then washed, drained, and dried in the air. It weighed 6.2 grams. After crystallising from 50 per cent. alcohol, and then twice from benzene, the substance was obtained in beautiful, golden, transparent prisms which melted at 130—131°. The substance, dried at 100°, gave the following results on analysis.

L 0.1185 gave 0.2920 CO, and 0.0630 H,O.

II. 0 0760 , 14.5 c.c. nitrogen at 22° and 764 mm. C = 67.22; H = 5.90; N = 21.15. $C_{15}H_{16}N_4O$ requires C = 67.16; H = 5.97; N = 20.89 per cent.

This product, therefore, exactly coincides with glycerosazone, $OH \cdot CH_2 \cdot C : N_2H \cdot C_6H_5$, which was obtained by Fischer and Tafel $CH : N_2H \cdot C_6H_5$

from 'glycerose' (Ber., 1887, 20, 1088, and 1888, 21, 2634), by Piloty and Ruff from dihydroxyacetoxime (Ber., 1897, 30, 1662), and by Piloty from dihydroxyacetone (Ber., 1898, 31, 3165).

The oxidation-product here obtained may, therefore, be dihydroxy-acetone, CO CH₂·OH, glyceraldehyde, OH·CH CH₂·OH, or, like Fischer's 'glycerose,' a mixture of these two.

'Glycerose,' obtained by the interaction of lead glyceroxide and bromine, was shown to consist for the greater part of dihydroxy-acetone; this was proved by the large yield of trihydroxyisobutyric acid obtained by the hydrogen cyanide reaction (Ber., 1889, 22, 110) and was later confirmed by Piloty (loc. cit., 3163) from the yield of dihydroxyacetoxime. The presence of glyceraldehyde was probable from the fact that, after separation of the trihydroxybutyric acid as calcium salt, lead acetate gave, in the mother liquor, a flocculent precipitate insoluble in hot water and in dilute acetic acid, differing in these respects from the trihydroxyisobutyrate. The quantity obtained by Fischer and Tafel was not sufficient for comparison with 'erythroglucic acid,' and, moreover, the properties of this latter acid are not at all characteristic.

A sharp distinction, however, between trihydroxyisobutyric acid and erythroglucic acid exists in the fact that the neutral salts of the former are not precipitated by normal lead acetate.

The product obtained in the present instance was further examined in the following way. About 50 grams of glycerol were exidised in

presence of iron in the manner described above, and the mixture, when cold, was well stirred with excess of barium carbonate; the solution, after filtration, was evaporated to a small bulk by distillation under greatly diminished pressure at 50°, concentrated to a syrup in a vacuum desiccator, and then mixed with several times its volume of absolute alcohol and a little ether. After being allowed to stand, it was filtered from barium and iron salts, the filtrate again allowed to evaporate in a vacuum desiccator, and the residue, dissolved in a little absolute alcohol, was mixed with about three times its volume of anhydrous ether; the precipitate was then allowed to settle, and the etheralcohol solution evaporated in a vacuum desiccator as before. No signs of crystallisation could be observed, however, even after repeating the alcohol-ether treatment and allowing the syrup to remain for several days in the vacuum, neither could crystallisation be brought about by cooling or by stirring with a drop of water. Piloty (Ber., 1898, 31, 3164) obtained crystallised dihydroxyacetone (from dihydroxyacetoxime); and Wohl (ibid., 2394), from the acetal of glyceraldehyde, obtained crystals corresponding in composition to the aldehyde. Wohl's crystalline compound, however, was shown by the cryoscopic method to have a 'double' formula, becoming 'single' when kept for some time in aqueous solution.

In the present case, therefore, it was not certain that crystallisation should be expected if the substance is glyceraldehyde, but the absence of crystallisation may very probably be due to the presence of impurities such as traces of barium or glycerol, which, by the above treatment, might not be wholly removed. In order to attack the problem, therefore, the method employed by Fischer and Tafel was followed; for this purpose, the purified syrup obtained in the manner above described was dissolved in 100 c.c. of water, and the reducing power of the solution estimated by Fehling's solution. The quantity available corresponded to 5.2 grams of glucose; this was mixed with 7 grams of anhydrous hydrogen cyanide and heated in a stoppered bottle, in a regulated bath, at 50° for 12 hours, and then for 12 hours more at 60°. The light brown solution was then evaporated somewhat in a vacuum to remove free hydrogen cyanide, the mixture placed in a freezing mixture, saturated with dry hydrogen chloride, and allowed to remain for 12 hours at 0°, and for 2 days more at the ordinary temperature; it was then evaporated as completely as possible on a water bath, the residue dissolved in about 200 c.c. of water, 45 grams of barium hydroxide, dissolved in hot water, added, and the mixture heated on a water bath. After a few minutes, a pale yellow, flocculent precipitate separated which was collected while hot, washed, and treated with a slight excess of hot dilute sulphuric acid; the filtered solution was very cautiously treated with baryta-water to remove the excess of sulphuric

acid, filtered, and the filtrate shaken with pure precipitated calcium carbonate. The clear liquid thus obtained was concentrated and allowed to stand for 4 days, but there were no signs of crystallisation, so that trihydroxybutyric acid appears to be either absent, or present in small quantity only. The solution of calcium salt was then decolorised with a little animal charcoal, and a solution of normal lead acetate added; a white, flocculent precipitate was produced which appeared to be insoluble in hot water or in acetic acid. This precipitate was well washed with hot water and dried at 160°.

I. 0.2593 gave 0.2303 PbSO₄. Pb = 60.67 per cent. II. 0.1190 , 0.1060 PbSO₄. Pb = 60.82 ,

Iamparter (Annalen, 184, 261) obtained erythroglucic acid by oxidation of erythritol with nitric acid, and, by precipitation of the free acid by excess of lead acetate, prepared the lead salt which, when dried at 160° , gave Pb= $61\cdot3$ per cent. The salt would appear, therefore, to have the composition $C_4H_6PbO_5$ (the lead replacing in a hydroxyl as well as the carboxyl group), for which theory requires Pb= $60\cdot70$ per cent.

Another portion of the ether-alcohol solution, prepared as before, was mixed with the calculated quantity of hydroxylamine in alcoholic solution, distilled to a small bulk under greatly reduced pressure, and kept in a vacuum desiccator; the syrup which was left showed practically no signs of crystallisation, even after long standing, stirring, &c. From the above results, it appears probable that the product of oxidation here obtained is chiefly, if not entirely, glyceraldehyde.

Erythritol.

Experiments with this substance were made in exactly the same manner as in the previous cases, and here again it was found that practically no action occurs in absence of ferrous iron; if present, however, there is energetic oxidation with considerable evolution of heat. The product strongly reduces Fehling's solution on warming, and restores the colour to a rosaniline salt bleached by sulphur dioxide. Phenylhydraxine acetate, after a short time, gives a beautiful, golden, flocculent precipitate, which increases in quantity on heating.

Ten grams of erythritol was dissolved in 300 c.c. of water, mixed with 5 grams of crystallised ferrous sulphate, and 50 c.c. of hydrogen dioxide slowly added as before; to the mixture, 25 grams of phenylhydrazin as acetate was then added, and the whole allowed to remain for 24 hours at the ordinary temperature. The precipitate, after being collected, washed, drained, and dried in the air, weighed 3.7 grams. The mother liquor was then heated on a water bath for 1½ hours, and the precipitate

collected, washed, and dried as before; it weighed 3.3 grams, so that the total yield was about 7 grams.

For analysis, the first product was selected, since that obtained by heating the mother liquor was somewhat discoloured and looked less pure. It was first heated with a large volume of water, in which it slowly dissolved, and the filtered solution deposited a golden, flocculent precipitate on cooling; this was collected, air-dried, and twice recrystallised from hot benzene, from which it separated in golden, microscopic needles.

After being dried at 100°, it melted sharply at 167°, and gave the following numbers on analysis.

0.0920 gave 0.2178 CO₂ and 0.0495 H_2O . C = 64.56; H = 5.91. Erythrosazone, $C_{16}H_{18}N_4O_2$, requires C = 64.43; H = 6.04 per cent.

From the good yield of osazone obtained in this experiment, the authors are encouraged to attempt the direct isolation of the oxidation product, and experiments will shortly be made in this direction.

Mannitol.

In this case, again, the presence of ferrous iron exerts a remarkable influence in bringing about the oxidation by hydrogen dioxide; a very considerable rise of temperature occurs, and the mixture, when cold gives an almost immediate precipitate with phenylhydrazine, and after separation of the iron, strongly reduces Fehling's solution on warming, In absence of ferrous iron, no such changes take place.

Twenty grams of pure recrystallised mannitol were dissolved in 100 c.c. of water, mixed with 5 grams of crystallised ferrous sulphate and 60 c.c. of hydrogen dioxide in the same manner as before. solution, after cooling, was made just alkaline with sodium carbonate, then acidified with acetic acid, and to the mixture 6 grams of phenylhydrazine as acetate were added. The separation of a yellow precipitate began after about 1 minute, and was allowed to continue for 1 hour; it was then collected, drained with the aid of the pump, washed, and allowed to dry in the air. The crude, orange-coloured substance, which weighed 12.5 grams, was purified by triturating it with a little acetone, draining with the pump, and crystallising from boiling water; the filtered solution, on cooling, deposited a yellowishwhite, crystalline precipitate, which was recrystallised from hot 60 per cent. alcohol, and twice again from hot water with the addition of a little animal charcoal. In this way, the product was obtained in the form of almost white, crystalline plates, which turn yellow at about 195° and melt fairly sharply at 197—198°. For analysis, the substance was dried at 100°.

I. 0.1206 gave 0.2345 CO₂ and 0.0710 H₂O. C = 53.29; H = 6.57.

II. 0·1020 gave 9·3 c.c. nitrogen at 17° and 756 mm. N = 10·55. Mannose hydrazone, $C_{12}H_{18}N_2O_5$, requires C = 53·33; H = 6·66; N = 10·39 per cent.

Direct Preparation of Mannose from Mannitol .- As the yield of hydrazone obtained in the manner just described appears to be considerably superior to that which results from the oxidation of mannitol by nitric acid, it became a matter of interest to ascertain whether the sugar could be prepared directly from the mixture obtained from oxidation, without previously isolating the hydrazone. Fifty grams of mannitol were dissolved in a small quantity of water, mixed with a solution of ferrous sulphate, and 150 c.c. of hydrogen dioxide added as previously described. The mixture was then treated with excess of freshly precipitated barium carbonate, filtered, the clear solution evaporated to a small bulk at about 50° under a pressure of about 30 mm., and the concentration then continued in a vacuum desiccator at the ordinary temperature until a thick syrup remained. This was treated with about ten times its volume of absolute alcohol, filtered, and an excess of anhydrous ether added to the clear filtrate; this caused the separation of a white, flocculent mass, which, on standing, collected to a light yellow syrup. After pouring off the liquid, the syrup was dissolved in a very small quantity of water, the solution exposed in a vacuum desiccator, and the syrupy residue thus obtained was rubbed with absolute alcohol and ether. when it was converted into a pasty mass, which became a greyishwhite, amorphous gum when kept in a vacuum over sulphuric acid. 0.36 gram of this product was dissolved in a little water, mixed with 0.5 gram of phenylhydrazine as acetate, and the mixture allowed to stand for one hour; a little absolute alcohol was then added and the precipitate collected on a weighed filter and dried at 100°. The weight of hydrazone obtained was 0.55 gram.

Wt. of substance: wt. of hydrazone obtained = 1:1.55. Theory requiring, mannose: hydrazone = 1:1.53.

The result, in fact, appears to be mannose in a pure, or nearly pure, state.

Dulcitol.

Exactly similar phenomena are observed when this substance is oxidised by hydrogen dioxide in presence of ferrous iron, the blank test giving negative results. Ten grams of dulcitol dissolved in 300 c.c. of water, was mixed with 5 grams of crystallised ferrous sulphate and 40 c.c. of hydrogen dioxide added. After cooling, 20 grams of phenylhydrazine as acetate was added, the mixture heated on

a water bath for one hour, and the yellowish, flocculent precipitate thus formed, when collected, washed, and air-dried, weighed 3.8 grams.

The crude osazone was rubbed with a little cold absolute alcohol, to remove resinous matter, and then twice recrystallised from hot absolute alcohol; the beautiful yellow leaflets thus obtained were dried a 100° and analysed.

0.1030 gave 0.2290 CO₂ and 0.0584 H₂O. C = 60.63; H = 6.29. $C_{18}H_{22}N_4O_4$ requires C = 60.33; H = 6.15 per cent.

The substance, when quickly heated, melted sharply at 206°, and appears, therefore, to be identical with that which Fischer and Tafel obtained by oxidising dulcitol with bromine (*Ber.*, 1887, 20, 3390).

Sorbitol.

Only a small quantity of this substance was available, but the results obtained were exactly analogous to those previously recorded. In presence of iron, heat was evolved and the solution then strongly reacted with phenylhydrazine, the blank experiment without iron showing practically no result.

0.7 gram of sorbitol was dissolved in water, mixed with a solution of 0.3 gram of ferrous sulphate, and 10 c.c. of hydrogen dioxide added; on adding phenylhydrazine acetate and heating the mixture on a water bath for one and a half hours, an osazone was obtained, which, after being washed, and recrystallised from ethylic acetate, melted sharply at 203°, and closely resembles glucosazone.

On analysis,

0.1190 gave 0.2625 CO₂ and 0.0672 H₂O. C = 60.19; H = 6.28. $C_{18}H_{22}N_4O_4$ requires C = 60.33; H = 6.15 per cent.

Oxidation in Presence of Sunlight.

In the case of tartaric acid, it was shown (*Brit. Assoc. Report*, 1895), that the oxidation to dihydroxymaleic acid may be brought about by atmospheric oxygen in presence of ferrous iron on exposure to sunlight; whilst in the absence of ferrous iron, or in the dark, practically no oxidation occurs. That the result was not due to atmospheric hydrogen dioxide or ozone was shown by using air previously purified by means of potassium iodide.

It is now found that a similar, although less rapid, result may be produced in the cases of glycol, glycerol, and erythritol. The oxidation products obtained with these substances in the manner described, all quickly restore the colour to a resamiline salt previously bleached

by sulphur dioxide, so that this test affords a delicate means of indicating the formation of such products. The experiments were made in the following way.

A solution of the alcohol was divided into three parts. To 1 and 2 a little ferrous sulphate, in solution, was added and 3 was left blank; 1 was kept in a dark cupboard, and 2 and 3 were exposed to sunlight for some hours. The three samples were then tested with the rosaniline solution, and, in the case of each of the above-named alcohols, a strongly marked coloration was produced in 2, that is, in the one exposed to sunlight in presence of iron, but practically none was obtained in 1 or in 3.

In the case of mannitol, dulcitol, &c., the results are uncertain, since the rosaniline test is inapplicable, and the characteristic reactions of the products of oxidation, such as with phenylhydrazine, are scarcely delicate enough for the purpose.

The greater part of the expense incurred in carrying out this and several previous investigations has been defrayed from grants kindly awarded by the Government Grant Committee of the Royal Society.

II.—β-Aldehydopropionic Acid, CHO·CH₂·CH₂·COOH, and β-Aldehydoisobutyric Acid, CHO·CH₂·CH(CH₈)·COOH.

By W. H. PERKIN, jun., and C. H. G. SPRANKLING.

Some time since (Trans., 1896, 69, 162), a paper was published by one of us in conjunction with Messrs. W. H. Bentley and E. Haworth which had for one of its objects the discovery of a method for introducing the group 'CH₂·CH₂·OH into organic substances, a synthetical process which, if it could be easily carried out, would be very valuable as a means of forming ring compounds. It was found that the action of glycol chlorhydrin, Cl·CH₂·CH₂·OH, on the sodium compounds of substances like ethylic acetoacetate, ethylic malonate, and their derivatives, did not, except in isolated cases, yield the desired result; ultimately, however, a method was devised which in the few cases tried gave fairly satisfactory results, and which may be briefly stated in the form of an example thus.

 β -Bromethyl phenyl ether, $C_6H_5\cdot O\cdot CH_2\cdot CH_2Br$, was prepared by acting on sodium phenoxide with ethylene bromide, and this, when digested with the sodium derivative of ethylic methylmalonate, yielded ethylic γ -phenoxyethylmalonate,

 $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot C(CH_8)(COOC_2H_5)_2$.

The acid corresponding to this ethereal salt, when heated at 100°, loses

one molecule of carbon dioxide with formation of γ-phenoxyethylmethylacetic acid, C₆H₅·O·CH₂·CH₂·CH(CH₃)·COOH, from which hydrobromic acid eliminates the phenyl group and forms γ-bromethylmethylacetic acid, CH₂Br·CH₂·CH(CH₃)·COOH. This brom-acid when boiled with sodium carbonate, gives the sodium salt of hydroxyethylmethylacetic acid, OH·CH₂·CH₂·CH(CH₃)·COONa, from which, on acidifying, methylbutyrolactone CH₂·CH₂·CH·CH₃, is at once obtained. When this method was tried in more complicated synthetical experiments, it did not work well, partly owing to the number of operations involved, but principally on account of the smallness of the yield obtained in some of these operations. For these reasons, experiments were made with a view to discover a more direct method, and ultimately we found in bromacetal, (C₂H₅O)₂CH·CH₂Br, a substance which seems likely to answer the purpose.

Bromacetal reacts readily with the sodium derivative of ethylic malonate, yielding sthylic acstalmalonate according to the equation

$$\begin{aligned} (\mathbf{C_2H_5O})_2\mathbf{CH}\cdot\mathbf{CH_2Br} + \mathbf{CHNa}(\mathbf{COOC_2H_5})_2 = \\ (\mathbf{C_2H_5O})_2\mathbf{CH}\cdot\mathbf{CH_2}\cdot\mathbf{CH}(\mathbf{COOC_2H_5})_2 + \mathbf{NaBr}. \end{aligned}$$

This ethylic salt, which distils without decomposition at $151-154^{\circ}$ (15 mm.), yields, on hydrolysis, the corresponding acetulmalonic acid, ($C_2H_5O)_2CH\cdot CH_2\cdot CH(COOH)_2$, and this, when heated with water at 180° is decomposed into alcohol, carbon dioxide, and β -aldehydopropionic acid, ($C_2H_5O)_2CH\cdot CH_2\cdot CH(COOH)_2 + H_2O = CHO\cdot CH_2\cdot CH_2\cdot COOH + 2C_2H_5\cdot OH + CO_2$. β -Aldehydopropionic acid is a new and very interesting substance, since it is the "half-aldehyde" of succinic acid and belongs to the class of aldehyde acids of which, so far, very few have been prepared. Its properties show that it is a true aldehyde, and not a hydroxymethylene compound of the formula

it therefore, does not belong to the class of substances which Claisen has investigated with such brilliant results. Aldehydopropionic acid is an almost colourless liquid which reduces Fehling's solution and gives a violet coloration with a solution of rosaniline hydrochloride decolorised by sulphurous acid. It is slowly oxidised in contact with air, rapidly by nitric acid, with formation of succinic acid, and when reduced with sodium amalgam it yields butyrolactons,

$$\mathbf{CHO} \cdot \mathbf{CH_2} \cdot \mathbf{CH_2} \cdot \mathbf{COOH} = \mathbf{OH} \cdot \mathbf{CH_2} \cdot \mathbf{CH_2} \cdot \mathbf{CH_2} \cdot \mathbf{COOH} = \begin{array}{c} \mathbf{CH_2} \cdot \mathbf{CH_2} \cdot \mathbf{CH_2} \\ \mathbf{O} & \mathbf{OOO} \end{array}$$

When boiled with caustic soda solution in a flat basin, aldehydopropionic acid undergoes a most interesting change, yielding small quantities of terephthalic acid, the dihydroterephthalic acid, which may be assumed to be the first product of the condensation, being oxidised to tere-

phthalic acid by the action of the air,

CHO·CH₂·CH₂·COOH CH·CH₂·C·COOH COOH·CH₂·CH₂·CHO = COOH·C·CH₂·CH CH·CH:C·COOH

and this is, so far, the only experiment which has been instituted with

the object of testing the value of aldehydopropionic acid in conden sation experiments.

The action of bromacetal on sodium compounds is probably a general

The action of bromacetal on sodium compounds is probably a general one, since we have found that the reaction proceeds equally well when the sodium derivative of ethylic methylmalonate is substituted for that of ethylic malonate in the above experiments.

The sthylic acstalmethylmalonate,

 $(\mathbf{C_2H_5O})_2\mathbf{CH} \cdot \mathbf{CH_2} \cdot \mathbf{C}(\mathbf{CH_3})(\mathbf{COOC_2H_5})_2,$

thus obtained yields acetalmethylmalonic acid,

 $(C_2H_5O)_2 \cdot CH \cdot CH_2 \cdot C(CH_8)(COOH)_2$

on hydrolysis, and this, when heated with water at 180°, is converted into β-aldehydoisobutyricacid, CHO·CH₂·CH(CH₃)·COOH, a liquid acid which, on oxidation, yields methyl succinic acid,

COOH·CH₂·CH(CH₃)·COOH.

Further experiments on the action of bromacetal on the sodium compounds of ethereal salts are in progress. It should be mentioned, in conclusion, that C. Harries (Ber., 1898, 31, 42) obtained a substance which is probably the methylal of the half-aldehyde of succinic acid, (CH₃O)₂CH·CH₂·COOH, by the action of sodium hypobromite on levulin methylal, (CH₃O)₂CH·CH₂·CO+CH₃·CO+CH₃, but he does not appear to have further investigated this substance.

Action of Bromacetal on the Sodium Derivative of Ethylic malonate.

Formation of Ethylic Acetalmalonate, (C₂H₅O)₂CH·CH₂·CH(COOC₂H₅)₂.

Ethylic acetalmalonate is conveniently prepared as follows. Sodium (14.2 grams) is dissolved in absolute alcohol (170 grams) and the solution, while still warm, is mixed with ethylic malonate (100 grams) and bromacetal (80 grams) and the mixture, inclosed in sealed tubes, is heated at 130—140° for 4 hours; when as much alcohol as possible has been removed from the product by distillation on the water bath, water is added to the residue and the precipitated oil extracted several times with ether. The ethereal solution is washed, well dried over calcium chloride, the ether distilled off, and the residual oil fractionated under reduced pressure (15 mm.). More than half passes over below 145° and consists of a mixture of unchanged ethylic malonate and bromacetal, whilst the fraction distilling between 145° and 165°

contains the ethylic acetalmalonate. The oil boiling below 145° (15 mm.), and which was assumed to contain about 50 per cent of bromacetal, was again heated in sealed tubes with the calculated quantity of the sodium derivative of ethylic malonate, the temperature, however, being now allowed to rise to 160°.

In this way, practically the whole of the bromacetal was converted into crude ethylic acetalmalonate boiling at 145—165° (15 mm.), and from this fraction the almost pure ethereal salt could be obtained by repeated fractionation as a colourless oil of a peculiar and not unpleasant odour, and boiling at 151—154° (15 mm.), or at 166—168° (at 26 mm.). Analysis.*

0.1821 gave 0.3714 CO₂ and 0.1418 H₂O. C = 55.62; H = 8.65. 0.1640 ,, 0.3360 CO₂ ,, 0.1282 H₂O. C = 55.87; H = 8.67. $(C_2H_5O)_2CH\cdot CH_2\cdot CH(COOC_2H_5)_2$ requires C = 56.50; H = 8.69 per cent.

Acetalmalonic Acid, (C₂H₅O)₂CH·CH₂·CH(COOH)₂.

Acetalmalonic acid is obtained by hydrolysing its ethereal salt with alcoholic potash, but the operation has to be carefully performed, since prolonged boiling with the alkali decomposes the acid with elimination of the group ${}^{\cdot}\mathrm{CH}(\mathrm{OC}_2\mathrm{H}_5)$, and formation of malonic acid. It is not clear how this decomposition takes place, but there can be no doubt as to the formation of malonic acid, since, in one instance, when a quantity of this acid was obtained melting at 131°, an analysis was carried out with the following results.

0.2687 gave 0.3480 CO_2 and 0.0972 H_2O . C=35.32; H=4.26. $CH_2(COOH)_2$ requires C=34.63; H=3.86 per cent.

It was very soluble in water, and when heated decomposed with evolution of carbon dioxide and formation of acetic acid.

If, however, the action of the potash is only allowed to proceed for a short time, hydrolysis takes place normally, and a good yield of acetalmalonic acid is obtained. After many experiments, we found that the following process gave the best results. Ten grams of the pure ethereal salt is mixed with a solution of 6 grams of pure potash in alcohol, and the mixture heated on the water-bath for 10 minutes, the alcohol is then rapidly driven off on the water-bath and the cold residue mixed with an excess of dilute sulphuric acid and extracted repeatedly with ether. The ethereal solution, after drying and evaporating, deposits a thick oil which shows no sign of crystallising, even after standing for some days over sulphuric acid in a vacuum. On

^{*} The numbers obtained are slightly low, on account of the oil containing traces of bromine, which it was found impossible to remove by fractionation.

andysis, it gave numbers agreeing approximately with those required for sectalmalonic acid.

```
I. 0·1150 gave 0·2040 CO<sub>2</sub> and 0·0722 H<sub>2</sub>O. C = 49 \cdot 15; H = 6 \cdot 97. II. 0·1779 ,, 0·3177 CO<sub>2</sub> ,, 0·1200 H<sub>2</sub>O. C = 48 \cdot 72; H = 7 \cdot 47. III. 0·1974 ,, 0·3529 CO<sub>2</sub> ,, 0·1227 H<sub>2</sub>O. C = 48 \cdot 75; H = 6 \cdot 91. IV. 0·1537 ,, 0·2719 CO<sub>2</sub> ,, 0·0915 H<sub>2</sub>O. C = 48 \cdot 26; H = 6 \cdot 61. (COOH)<sub>2</sub>CH·CH<sub>2</sub>·CH(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> requires C = 49 \cdot 05; H = 7 \cdot 27 per cent.
```

Silver salt.—Acetalmalonic acid is very soluble in water, and if the aqueous solution is neutralised with ammonia, and silver nitrate added, a dense, white precipitate of the silver salt is precipitated, which, after washing first with water and then with alcohol and ether, gave the following results on analysis.

```
0.2177 gave, on ignition, 0.1092 Ag. Ag = 50.16. (C_2H_5O)_2CH\cdot CH_2\cdot CH(COOAg)_2 requires Ag = 49.79 per cent.
```

Distillation of Acetalmalonic Acid.—When this acid is heated in a fractionating flask, decomposition soon sets in with evolution of carbon dioxide, and the residue, after repeatedly fractionating under reduced pressure, yields a liquid which boils, apparently constantly, at 157—161° (15 mm.), and which was at first thought to be acetalacetic acid (C₂H₅O)₂CH·CH₂·COOH. The analyses, however, show that this substance consists, for the most part, of aldehydopropionic acid (p. 16), elimination of alcohol having taken place during the distillation owing, probably, to the unavoidable presence of small quantities of water.

```
0.2658 gave 0.4740 CO<sub>2</sub> and 0.1607 H<sub>2</sub>O. C=48.63; H=6.71.
0.2514 ,, 0.4372 CO<sub>2</sub> ,, 0.1437 H<sub>2</sub>O. C=48.53; H=6.39.
COOH·CH<sub>2</sub>·CH<sub>2</sub>·CHO requires C=47.05; H=5.88 per cent.
COOH·CH<sub>2</sub>·CH<sub>2</sub>·CH(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> requires C=54.54; H=9.09 per cent.
```

In order to confirm this view, the liquid was heated with an equal quantity of phenylhydrazine for 10 minutes at 150° and poured into ether, when, on standing, a white, crystalline substance separated, which, after crystallisation from acetic acid, melted at 191° and gave the following results on analysis.

```
0.0601 gave 0.1502 CO<sub>2</sub> and 0.0350 H<sub>2</sub>O. C = 68.17; H = 6.47. 0.1258 gave 21.3 c.c. nitrogen at 19° and 768 mm. N = 19.42. C_{16}H_{16}N_{4}O requires C = 68.09; H = 6.38; N = 19.85 per cent.
```

This substance, on examination, was found to be identical with the condensation product formed by heating aldehydopropionic acid with

The four analyses given here were carried out with four different preparations of the acid.

phenylhydrazine (see below), and thus it is probable that this aldehydoacid was present in the oil obtained by the distillation of acetalmalonic acid.

β-Aldshydopropionic acid, CHO·CH₂·CH₂·COOH.

In order to prepare this substance, acetalmalonic acid is heated with about four times its weight of water at 180—190° for 4 hours, the solution evaporated on the water-bath, and the residue allowed to stand over sulphuric acid in a well exhausted desiccator for 4 or 5 days.

The yellow, oily residue thus obtained, on analysis, gave numbers agreeing approximately with those required for β -aldehydopropionic acid.*

```
I. 0.2084 gave 0.3611 CO<sub>2</sub> and 0.1127 H<sub>2</sub>O. C = 47.40; H = 6.01. II. 0.2124 ,, 0.3675 CO<sub>2</sub> ,, 0.1132 H<sub>2</sub>O. C = 47.20; H = 5.92. III. 0.1703 ,, 0.2928 CO<sub>2</sub> ,, 0.0890 H<sub>2</sub>O. C = 46.89; H = 5.82. IV. 0.1379 ,, 0.2300 CO<sub>2</sub> ,, 0.0806 H<sub>2</sub>O. C = 45.47; H = 6.47. V. 0.1576 ,, 0.2649 CO<sub>2</sub> ,, 0.0909 H<sub>2</sub>O. C = 45.90; H = 6.40. CHO·CH<sub>2</sub>·CH<sub>2</sub>·COOH requires C = 47.05; H = 5.88 per cent.
```

β-Aldehydopropionic acid is a slightly brownish liquid which dissolves readily in water, freshly prepared, its solution reduces Fehling's solution, and produces a pink colour when mixed with a solution of rosaniline hydrochloride which has been decolorised with sulphur dioxide. When heated at 150° with phenylhydrazine for 10 minutes, condensation readily takes place, and if the product is poured into ether a white, crystalline substance separates on standing, which, after recrystallisation from acetic acid, gave the following results on analysis.

```
0.0590 gave 10.1 c.c. nitrogen at 18^{\circ} and 758 mm. N = 20.00.
```

This substance, of which a full analysis is given on p. 15, melts at 192° and is evidently the phenylhydrazide of the phenylhydrazone of aldehydopropionic acid, C₆H₅·NH·N:CH·CH₂·CH₂·CO·NH·NH·C₆H₅, which contains 19.85 per cent. of nitrogen.

Oxidation of Aldehydopropionic Acid. Formation of Succinic Acid.

When aldehydopropionic acid is left exposed to the air, it darkens in colour and gradually deposits crystals, ultimately being converted into a brown, pasty mass, which in contact with porous porcelain slowly

* As this substance would not crystallise, analyses of each preparation were made, and some of these varied as much as 3 per cent. from the theoretical; we therefore wish it to be distinctly understood that we do not consider that the aldehydo-acid made in this way is pure. All the preparations contained a small amount of ash derived from the tube in which they were prepared; this was allowed for in the analyses.

becomes a nearly colourless, crystalline mass, the sticky, oily impurity being only very gradually absorbed.

The crystals were purified by recrystallisation from hydrochloric acid with the aid of animal charcoal, and in this way colourless plates were obtained which melted at 181° and had all the properties of succinic acid. Analysis.

0.1201 gave 0.1786 CO_2 and 0.0561 H_2O . C=40.56; H=5.18. $COOH\cdot CH_2\cdot CH_2\cdot COOH$ requires C=40.68; H=5.08 per cent.

This experiment shows that aldehydopropionic acid is slowly converted into succinic acid by the oxygen of the air, and this change takes place very rapidly when oxidising agents are employed. A small quantity of the aldehydo-acid, after being heated to boiling with dilute nitric acid (20 per cent.) for some hours until no further oxidation took place, was evaporated repeatedly on the water-bath with the addition of small quantities of water, until a colourless, crystalline residue was left. This, after recrystallisation from hydrochloric acid, melted at 181—184° and consisted of succinic acid.

0-0598 gave 0-0898 CO₂ and 0-0279 H_2O . C = 40.96; H = 5.18. COOH-CH₂-CH₂-COOH requires C = 40.68; H = 5.08 per cent.

Five grams of the pure aldehydo-acid were dissolved in water and treated with three times the calculated quantity of 4 per cent. sodium amalgam, carbon dioxide being passed through the liquid and the temperature kept below 10° during the whole operation, in order to avoid, as far as possible, risk of polymerisation or condensation; after separating the mercury, the solution was made strongly acid with sulphuric acid, heated to boiling for half an hour in a reflux apparatus, and then repeatedly extracted with ether. The ethereal solution, when dried and evaporated, deposited a colourless oil, which, after twice fractionating, boiled at 203—208°. On analysis, it gave numbers agreeing with those of butyrolactone, which, according to Fittig and Roeder (Annalen, 227, 1885, 22), boils at 206°.

0.1356 gave 0.2760 CO₂ and 0.0888 H₂O. C = 55.51; H = 7.27. $C_4H_6O_2$ requires C = 55.81; H = 6.97 per cent.

Action of Caustic Soda on β-Aldehydopropionic Acid. Synthesis of Terephthalic Acid.

This synthesis, which is explained in the introduction to this paper, was carried out as follows. β-Aldehydopropionic acid (10 grams) was dissolved in an excess of dilute sodium hydroxide and the solution evaporated in a flat glass basin nearly to dryness, water was then added and the solution again evaporated, this operation being continued during three days; the concentrated liquid, after being acidified and allowed to stand over-night, deposited a small quantity of a brownish powder, which, on examination, was found to be crude terephthalic acid. This was purified by dissolving it in dilute sodium carbonate, boiling with animal charcoal until most of the colour had been removed, and then treating the solution at 0° with permanganate until the violet colour remained permanent for 2 minutes; the filtrate from the manganese precipitate was concentrated, and, while still hot, acidified with hydrochloric acid; the colourless, crystalline precipitate. which separated rapidly, had all the properties of terephthalic acid. It was almost insoluble in water and ether, did not melt at 270°, and on heating in a small test tube it sublimed apparently without melting.

The small quantity of acid remaining (about 0.2 gram) was converted into its methylic salt by Baeyer's (Annalen, 1888, 245, 140) method by heating with phosphorus pentachloride, mixing the product with methylic alcohol, and purifying the crystals which separated, by recrystallisation from methylic alcohol, with the aid of animal charcoal; the colourless plates thus obtained were very sparingly soluble in methylic alcohol and melted sharply at 140°, the melting point of the methylic salt of terephthalic acid. A specimen of the methylic salt prepared from pure terephthalic acid was found to be identical with the synthetical substance in every respect, moreover, an intimate mixture of the two preparations melted sharply at 140°. These experiments prove conclusively that the acid formed by the action of sodium hydroxide on β -aldehydopropionic acid is terephthalic acid, and it is unfortunate that, in spite of a number of experiments, we have been unable to devise a better method for the condensation of the aldehyde, as the yield of terephthalic acid obtained was certainly not more than 5 per cent.

β-Aldshydoisobutyric Acid, CHO·CH₂·CH(CH₈)·COOH.

The first step in synthesising this substance was to prepare ethylic acetalmethylmalonate, and this was readily accomplished by heating the sodium derivative of ethylic methylmalonate with bromacetal

under the conditions already described in the case of ethylic acetalmalonate. The ethylic malonate employed in these experiments was made by the etherification of pure methylmalonic acid; the quantities of the substances used in the synthesis of ethylic acetalmethylmalonate were,

Ethylic methylmalonate	54 g	rams.
Sodium	7.2	, 93
Bromacetal	40	39

After isolating the product in the way described in the case of ethylic acetalmalonate, the crude oil was submitted to careful fractionation and the fraction 165° (26 mm.), which consisted of nearly pure ethylic acetalmethylmalonate, was analysed with the following result.

0.1491 gave 0.3056 CO₂ and 0.1204 H₂O. C = 57.20; H = 8.97. $(C_2H_5O)_2CH \cdot CH_2 \cdot CH(CH_3)(COOC_2H_5)_2$ requires C = 57.92; H = 8.96 per cent.

Acetalmethylmalonic Acid, (C2H5O)2·CH·CH2·CH(CH2)(COOH)2.

This acid, which was prepared by the careful hydrolysis of its ethereal salt, is a colourless syrup readily soluble in water.

0.1965 gave 0.3624 CO₂ and 0.1404 H₂O. C = 50.30; H = 7.94. $C_{16}H_{18}O_6$ requires C = 51.28; H = 7.69 per cent.

The silver salt, prepared by precipitating a neutral solution of the ammonium salt with silver nitrate, is a white, amorphous powder, which readily darkens when exposed to light.

0.2026 gave, on ignition, 0.0980 Ag. Ag = 48.37. $C_{10}H_{10}Ag_{2}O_{4}$ requires Ag = 48.19 per cent.

Aldehydoisobutyric acid, obtained by heating acetalmethylmalonic acid with water at 180° for 4 hours, and evaporating the liquid on a water bath, is an oil which, after standing for some days over sulphuric acid in a vacuum, was analysed with the following results.*

0.1933 gave 0.3653 CO₂ and 0.1238 H₂O. C = 51.53; H = 7.28. CHO-CH₂-CH(CH₃)-COOH requires C = 51.72; H = 6.89 per cent.

This substance is very similar to aldehydopropionic acid in its preperties, and its constitution is proved by the fact that, when oxidised with nitric acid, it yields *methylsuccinic* acid; this, after recrystallisation, melted at 110—112°, and gave the correct numbers on analysis.

0.2142 gave 0.3558 CO₂ and 0.1238 H_2O . C = 45.30; H = 6.40. COOH-CH(CH₂)·CH₂·COOH requires C = 45.45; H = 6.06 per cent.

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^{*} See footnote, p. 16.

III.—Cannabinol. Part I.

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In a paper communicated to the Society in 1896 (Trans., 1896, 69, 539) the authors, under the name of "cannabinol," described a physiologically active substance which they had isolated from "charas," the exuded resin of Indian hemp. From the constancy of composition of a number of preparations of this substance obtained from different samples of "charas," it was believed to be a definite chemical compound of the formula $C_{18}H_{24}O_2$; this conclusion seemed to be justified by the determination of the molecular weight, and by the examination of several derivatives. Since then, the authors have further examined cannabinol, and have found that it is a mixture of at least two compounds having similar physical characters. One of these, of the formula $C_{21}H_{26}O_2$, has been isolated, and it is proposed to retain the name cannabinol for this compound.

During the progress of this investigation, a note on oxycannabin by . Messrs. Dunstan and Henry appeared in the Proceedings of the Society (Proc., 1898, p. 44), in which the formulæ $C_{10}H_{10}NO_4$ and $C_{18}H_{25}OAc$ were assigned to oxycannabin and acetylcannabinol respectively. From the description of these substances, there can be no doubt that they are identical with those we have obtained, but the results of our analyses correspond with the formulæ $C_{11}H_{11}NO_4$ for oxycannabin and $C_{21}H_{25}O_2 \cdot C_2H_8O$ for acetylcannabinol. These formulæ are confirmed by molecular weight determinations, and by analyses of many derivatives. Dunstan and Henry (loc. cit.) state that, on oxidising cannabinol with nitric acid, normal butyric acid is formed; we can confirm this statement, with the addition that larger quantities of normal valeric and caproic acids are produced at the same time.

As the present paper deals mainly with the substances produced by the breaking down of the cannabinol molecule, the authors have only described such of its reactions as suffice to show that it is a true chemical compound. An account of the reactions of cannabinol, together with a more complete examination of several of the compounds described below, will shortly be brought before the Society.

When crude cannabinol (the red oil obtained by fractionating alcoholic charas extract under diminished pressure) is treated with nitric acid under certain conditions, it yields a yellow, crystalline substance, the analysis of which corresponds with the formula $C_{18}H_{16}N_2O_6$ (Proc., 1898, p. 66), but determinations of the molecular weight show that a higher formula is required. As it has acidic

properties, salts were prepared and analysed, and their composition proves that the formula is $C_{21}H_{22}N_3O_3$, which agrees with the molecular weight determinations. It is readily reduced by boiling with hydriodic acid and phosphorus, yielding the hydriodide of a base; the latter has not as yet been isolated, owing to the readiness with which it oxidises. As the formula $C_{21}H_{23}N_3O_3$ represents the trinitroderivative of a compound, $C_{21}H_{26}O_2$, the presence of the latter in crude cannabinol is probable, and this is definitely proved by the isolation of the acetyl derivative, $C_{21}H_{22}O_4 \cdot C_2H_2O_4$, from a crude cannabinol.

After the separation of the crystalline acetyl derivative from the products obtained by the acetylation of crude cannabinol, an oily residue was left amounting to more than three-quarters of the acetylation product, and from it by treatment with acetic anhydride, no other crystalline acetyl derivative could be obtained; it appears to contain the acetyl derivatives of one or more substances with a lower percentage of carbon than $C_{21}H_{26}O_{2}$.

"Crude cannabinol" is, therefore, a mixture of cannabinol, $C_{21}H_{26}O_2$, with one or more compounds probably of lower molecular weight.

The fact that cannabinol forms an acetyl derivative proves that it contains a hydroxylic group, and the failure of all attempts to obtain an ethereal salt from the trinitro-compound referred to above, makes it probable that the acidity of the latter is not due to the presence of a carboxyl group, but to the influence of the nitro-groups on the hydroxyl group.

On oxidising the trinitro-derivative by boiling it for several hours with fuming nitric acid, and pouring the product into water, a yellow, flocculent precipitate was deposited; this was filtered off, and the acid filtrate steam distilled; the distillate was found to contain normal butyric, valeric, and caproic acids. The normal butyric acid was identified by its calcium salt, the normal valeric and caproic acids by their anilides. By direct oxidation of crude cannabinol with nitric acid, the same fatty acids were obtained, and caproic acid was also obtained when potassium permanganate or chromic acid mixture was employed.

The yellow, flocculent precipitate, on crystallisation, gave a mixture of oily acids containing nitrogen, and a pale yellow, crystalline compound, the oxycannabin of Bolas and Francis (Chem. News, 1871, 24, 77); to this they gave the formula $C_{20}H_{20}N_2O_7$, but the results of their analyses agree equally well with the authors' formula $C_{11}H_{11}NO_4$. Dunstan and Henry, in their note (Proc., loc. cit.), state that oxycannabin "does not dissolve in aqueous alkalis unless warmed with them in a closed tube. By acidifying the resulting solution, an acid is precipitated which is at present under investigation. Oxycannabin would, therefore, appear to be a lactone." The present authors find,

however, that oxycannabin dissolves in aqueous caustic soda if boiled with it for a few minutes, and that unaltered oxycannabin is precipitated on acidification. They have proved it to be a lactone by the preparation and analysis of salts of the corresponding oxy-acid, but this oxy-acid has not been isolated, since it is at once re-converted into the lactone when set free from its salts. In fact, its tendency to undergo this change is so great that, on treating the silver salt with ethylic iodide, the lactone is obtained instead of the ethylic salt.

On oxidation with dilute nitric acid at 185°, oxycannabin yields a sparingly soluble nitro-lactonic acid of the formula C₁₀H₈NO₄·COOH together with a very soluble tribasic acid, C₉H₈NO₈.

On reduction, oxycannabin yields a compound, $C_{11}H_{13}NO_9$, which corresponds to the reduction of a nitro-group in oxycannabin to an amido-group. On this evidence, the authors propose for oxycannabin the name nitrocannabino-lactone, and for the reduction product the name amidocannabino-lactone.

The amido-lactone is readily diazotised, and an attempt was made to prepare cannabino-lactone directly from it by Friedländer's method, but it was found more convenient to prepare iodocannabino-lactone, $C_{11}H_{11}IO_2$, by adding potassium iodide to the diazotised solution, and to reduce this with sodium amalgam in alkaline solution. The oily cannabino-lactone, $C_{11}H_{12}O_2$, thus obtained, was converted into colourless crystalline, cannabino-lactonic acid, $C_{11}H_{10}O_4$, by boiling it with an alkaline solution of potassium permanganate; this action corresponds to the oxidation of a methyl group to a carboxyl group. On reduction with hydriodic acid and phosphorus, the lactonic acid yields a dibasic acid of the formula $C_{11}H_{12}O_4$, thus affording confirmation of its lactonic nature.

From the fact that a methyl group, both in cannabino-lactone and in its nitro-derivative, is oxidised to a carboxyl group, and from the behaviour of nitrocannabino-lactone on reduction, and subsequent diazotisation, the presence of a benzene nucleus in cannabino-lactone is probable. In order to confirm this, and, further, to ascertain the structure of the lactone ring, the lactonic acid was fused with caustic potash; in this way, isophthalic acid was obtained, and identified by conversion into its methylic salt. However, when cannabino-lactone was fused with potash, metatoluic acid was formed, together with isophthalic acid. The formation of these two acids definitely proves the presence in cannabino-lactone of a benzene nucleus, with two stide chains in the meta-position relatively to each other, one of these chains being a methyl group. The second side chain must evidently contain the lactone ring, and on the assumption that it is a γ -lactone, which from its great stability is probable, there appear to

be only three possible formulæ, namely, those of the three metatolylbutyrolactones,

Syntheses of these three lactones are at present in progress, with a view to deciding which of them is identical with cannabino-lactone.

The following table shows the relationships of the compounds described in this paper.

Cannabinol, $C_{21}H_{25}O_3$.

Acetylcannabinol, $C_{21}H_{25}O_3 \cdot COCH_3$.

Trinitrocannabinol, $C_{21}H_{25}O_3 \cdot COCH_3$.

Cannabino-lactone, (1) $CH_3 \cdot C_6H_4 \stackrel{C_2H_5}{\longrightarrow} CO(3)$.

Nitrocannabino-lactone (oxycannabin), (1) $CH_3 \stackrel{C}{\longrightarrow} C_6H_3 \stackrel{C_3H_5}{\longrightarrow} CO$ Amidocannabino-lactone, (1) $CH_3 \stackrel{C}{\longrightarrow} C_6H_3 \stackrel{C_3H_5}{\longrightarrow} CO$ (3).

Iodocannabino-lactone, (1) $CH_3 \stackrel{C}{\longrightarrow} C_6H_3 \stackrel{C_3H_5}{\longrightarrow} CO$ (3).

Cannabino-lactonic acid, (1) $COOH \cdot C_6H_4 \stackrel{C_3H_5}{\longrightarrow} CO$ (3).

Nitrocannabino-lactonic acid, (1) $COOH \cdot C_6H_4 \stackrel{C_3H_5}{\longrightarrow} CO$ (3).

Carboxyphenylbutyric acid, $COOH \cdot C_6H_4 \cdot C_3H_4 \cdot COOH$ (3).

EXPERIMENTAL.

Trinitrocannabinol, $C_{si}H_{ss}(NO_3)_sO_s$.—This compound is produced on adding fuming nitric acid (5 c.c.), drop by drop, to a well cooled solution of crude cannabinol (8 grams), dissolved in glacial acetic acid (18 c.c.), the temperature being kept down by immersing the flask in ice cold water. After standing for several days, the crystals are collected; the yield is 20 per cent. (1.6 grams) of the crude cannabinol used. The compound is easily soluble in benzene, phenol, alcohol, and ether; it is also readily soluble in hot, but only sparingly in cold, glacial acetic acid, which is the most convenient solvent for its recrystallisation. It crystallises in bright yellow plates, which, when quickly heated, melt at 160° (uncorr.) with some decomposition.

Four preparations were analysed

A and B, purified through the ammonium salt. C. Five times recrystallised from glacial acetic acid. D. Sample C, once recrystallised from alcohol.

A. $\begin{cases} 0.1417 \text{ gave } 0.2935 \text{ CO}_2 \text{ and } 0.0678 \text{ H}_2\text{O}. \\ 0.1235 & \text{,} 10 \text{ c.c. moist nitrogen at } 18^\circ \end{cases}$., 10 c.c. moist nitrogen at 18° and 760 mm.

B. 0·1676 ,, 0·3480 CO₂ and 0·0835 H₂O.
C. {0·1860 ,, 0·3855 CO₂ ,, 0·0913 H₂O.
(0·1440 ,, 11·5 c.c. moist nitrogen at 21° and 756 mm.

D. 0.1527 , 0.3180 CO₂ and 0.0750 H₂O.

Calculated for Found.			ınd.				
	Han,			A.	В.	C.	D.
C= 1	56.6 p	er ce	at	56.5	56.6	56.5	56.8
$\mathbf{H} =$	5.2	,,		5.3	5.5	5.4	5.5
N =	9.4	••		9.3		9.0	

The molecular weight was determined by the freezing point method in benzene and in phenol.

In benzene (i) 0.5220 gram, dissolved in 20 grams of benzene, lowered the freezing point by 0.312°.

(ii) 0.9513 gram, dissolved in 20 grams benzene, lowered the freezing point by 0.570°.

In phenol (iii) 0.4733 gram, dissolved in 20 grams phenol, lowered the freezing point by 0.410°.

(iv) 1.0023 grams, dissolved in 20 grams phenol, lowered the freezing point by 0.900°.

Calculated for	Found.			
$C_{20}H_{22}N_{2}O_{8}$.	(i).	(ii).	(iii).	(iv).
Molecular weight = 445	409	409	427	412

Salts.—The compound has acidic properties, forming salts of potassium, sodium, ammonium, and silver, all of which are bright yellow, crystalline compounds sparingly soluble in water, easily in alcohol. They are best crystallised by diluting their hot alcoholic solutions with water. The potassium and sodium salts are explosive, the silver salt is not.

Sodium Salt.—The most soluble of all the salts examined, the saturated solution at 15° containing 1 part of salt in 120 parts of solution. It is prepared by dissolving the acid in excess of alcoholic soda solution and diluting with water. Two samples were analysed.

0.2130, at 160° , lost $0.0290 \text{ H}_2\text{O}$ and gave $0.0255 \text{ Na}_2\text{SO}_4$. Na = 3.9; $H_0O = 13.6$.

0.1545 gave 0.0205 Na₂SO₄. Na = 4.3.

 $NaC_{21}H_{22}N_{3}O_{8} + 4H_{2}O$ requires Na = 4.3; $H_{2}O = 13.4$ per cent.

Potassium salt, prepared in the same way as the sodium salt, equires for solution 2000 parts of water at 15°, and 500 at 100°.

. 0.1210 lost no weight at 150°, and gave 0.0220 K_0SO_4 . K=8.2. $0.1300 \text{ gave } 0.230 \text{ K}_2\text{SO}_4$; K = 7.9.

 $KC_{21}H_{22}N_3O_8$ requires K=8.1 per cent,

Ammonium salt may be prepared by dissolving the acid in boiling ammonia solution, when the salt crystallises out on cooling, or by dissolving the acid in excess of alcoholic ammonia and diluting with water. It requires for solution 1600 parts of water at 15°, and 200 at 100°.

Silver salt, prepared either by adding silver nitrate solution to the solution of the sodium salt, or by boiling the alcoholic solution of the acid with excess of silver carbonate. A. Was prepared from the sodium salt and recrystallised from alcohol. B. From the acid and silver carbonate. C is B recrystallised.

$$\begin{array}{l} A. & \left\{ \begin{array}{l} 0.1900 \text{ gave } 0.3180 \text{ CO}_2, \ 0.0715 \text{ H}_2\text{O}, \ \text{and } \ 0.0362 \text{ Ag. } \ C=45.6 \ ; \\ H=4.2 \ ; \ Ag=19.1. \\ 0.1829 \text{ gave } 11.2 \text{ c.c. moist nitrogen at } 16^{\circ} \text{ and } 766 \text{ mm. } \ N=7.2. \\ B. \quad 0.1580 \quad , \quad 0.2673 \text{ CO}_2, \ 0.0586 \text{ H}_2\text{O} \text{ and } 0.0295 \text{ Ag. } \ C=46.1 \ ; \\ H=4.1 \ ; \ Ag=18.8. \\ \left\{ \begin{array}{l} 0.1850 \text{ gave } 0.3090 \text{ CO}_2, \ 0.0675 \text{ H}_2\text{O} \ , \quad 0.0357 \text{ Ag. } \ C=45.5 \ ; \\ H=4.1 \ ; \ Ag=19.3. \\ 0.2600 \text{ gave } 16.2 \text{ c.c. moist nitrogen at } 18^{\circ} \text{ and } 758 \text{ mm. } \ N=7.2. \\ AgC_{11}H_{12}N_{2}O_{3} \text{ requires } C=45.6 \ ; \ H=4.0 \ ; \ N=7.6 \ ; \ Ag=19.4 \text{ per cent.} \end{array} \right.$$

Reduction of Trinitrocannabinol.—Trinitrocannabinol is reduced by boiling with hydriodic acid and phosphorus in acetic acid solution; 3.7 grams of trinitrocannabinol were dissolved in 50 c.c. of glacial acetic acid, and boiled for 1½ hours with 25 c.c. of hydriodic acid sp. gr. 1.6, and 4 grams of yellow phosphorus; the almost colourless solution was then filtered from the excess of phosphorus, and distilled down to one-third its volume. The pale yellow crystals of hydriodide which were deposited on cooling were collected, washed with acetic acid, and dried in a vacuum over solid potash.

Attempts to isolate the base failed, as when set free from the hydriodide it is at once oxidised, with formation of coloured products.

The hydriodide was analysed, and gave the following numbers, C = 41.2; H = 5.2; I = 41.3; N = 5.0 per cent.

The authors do not feel justified in making any statement as to the constitution of the product of reduction until they have isolated the base and made a further examination.

Acetylcannabinol, C21H25O2 CO CH3.—Crude cannabinol is readily

acetylated by boiling it with acetic anhydride or with acetic chloride. After distilling off the excess of acetic anhydride and rectifying the residue under diminished pressure, an oil, lighter in colour and more mobile than the original crude cannabinol, is obtained; this sometimes, on standing, but, better, by dissolving it in alcohol and cooling the solution to 0° , deposits a white, crystalline substance, which can be purified by crystallisation from alcohol, light petroleum, or acetic acid; it melts at 75° , and is evidently identical with the 'acetylcannabinol, $C_{18}H_{23}OAc$,' mentioned by Dunstan and Henry (loc. cit.).

Analysis indicated as the simplest formula $C_{18}H_{18}O_2$ (Proc., 1898, 66), but determination of the molecular weight and the results of saponification show that the higher formula, $C_{23}H_{28}O_3$, must be adopted (Proc., 1898, 153).

The following samples were analysed. A. Recrystallised from alcohol. B. Four times recrystallised from alcohol. C. Recrystallised from light petroleum and then from acetic acid.

 $C_{18}H_{28}O_2 \cdot CO \cdot CH_3$ requires C = 78.4; $H_2O = 8.0$ per cent. $C_{18}H_{28}OAc$ (Dunstan and Henry) requires C = 80.5; H = 8.7 per cent.

The molecular weight was determined by the freezing point method, in glacial acetic acid and in benzene.

In glacial acetic acid.—(i) 0.2043 gram, dissolved in 20 grams of glacial acetic acid, caused a depression of 0.123°.

(ii) 0.5052 gram, dissolved in 20 grams of glacial acetic acid, caused a depression of 0.310°.

In benzene.*—(iii) 0·1877 gram, dissolved in 17·04 grams of benzene, caused a depression of 0·140°.

(iv) 0.3032 gram, dissolved in 17.04 grams of benzene, caused a depression of 0.240° .

Calculated for	Calculated for Found.				
C ₁₅ H ₁₈ O ₂ .	CuH203.CO.CH3.			(iii).	
Mol. wt. = 230	352	324	318	385	365.

The percentage of acetyl was determined by saponifying the compound, either by boiling with alcoholic potash, or by heating with it in a sealed tube at 130°. Water was added to the product,

^{*} For the molecular weight determination in benzene solution, we are indebted to the kindness of Mr. H. Jackson, B.A., Downing College.

and, after the alcohol had been boiled off, the solution was made strongly acid with phosphoric acid, and steam distilled until the distillate no longer had an acid reaction. The distillate was then titrated with semi-normal caustic soda solution.

1.6 gave acetic acid equivalent to 8.85 c.c. N/2 NaOH solution.

9.0 , , 52.4 c.c.

Calculated for Calculated for $C_{15}H_{18}O_{2}$, $C_{n1}H_{26}O_{2}$ $CO^{*}CH_{3}$. Found., Acetyl=18.7 per cent. 12.2 11.9, 12.5.

Cannabinol, C₂₁H₂₆O₂.

The residues left in the distilling flasks in the above acetyl determinations were extracted with ether. The ethereal solution was dried over calcium chloride, the ether distilled off, and the residue distilled under diminished pressure, when practically the whole passed over at 285° under 80 mm. pressure; the distillate was an almost colourless oil, which, on cooling, set to a transparent resin. A second preparation was made, and both were analysed.

0.1880 gave 0.5587 CO₂ and 0.1445 H₂O. C = 81.5; H = 8.5. 0.1715 , 0.5100 CO₂ ,, 0.1300 H₂O. C = 81.1; H = 8.4. $C_{11}H_{12}O_{12}$ requires C = 81.3; H = 8.4 per cent.

The molecular weight was found by the freezing point method in glacial acetic acid solution.

0.5876 gram, in 20 grams of glacial acetic acid, gave a depression of 0.380°.

0.6250 gram, in 20 grams of glacial acetic acid, gave a depression of 0.390°.

Calculated for $C_{21}H_{22}O_{2}$. Found. Mol. wt. = 310. 310, 313.

The compound is optically inactive.

Oxidation of Trinitrocannabinol with Nitric Acid.

One hundred and twenty grams of trinitrocannabinol was dissolved in 300 c.c. of hot, fuming nitric acid, and gently boiled for 5 hours in a reflux apparatus, more acid being added from time to time, until in all 700 c.c. had been used. On pouring the product into water, 70 grams of a yellow, waxy precipitate separated, and from this 35 grams of nitrocannabino-lactone (oxycannabin) were obtained on treatment with alcohol. The filtrate from the above yellow precipitate

smelt strongly of valeric acid, and contained normal caproic, valeric, and butyric acids, possibly also propionic acid, together with non-volatile acids. Substantially the same products were obtained by the oxidation of crude cannabinol with nitric acid.

Examination of the Volatile Fatty Acids.

The volatile acids were removed from the above-mentioned acid mother liquor by steam distillation, and the distillate neutralised with sodium carbonate and evaporated to dryness; on acidifying with dilute sulphuric acid and extracting with ether, 12 grams of the mixed acids were obtained. These were fractionated with the following results.

$$105-150^{\circ}=2.2$$
 grams. $170-180^{\circ}=1.2$ grams. $150-170^{\circ}=0.9$, $180-195^{\circ}=3.9$,, Above $195^{\circ}=1.85$ grams.

From the fraction 150—170°, normal butyric acid was isolated by means of its calcium salt, which was purified and analysed, with the following results.

```
0.0730 lost 0.0037 H_2O at 135° and gave 0.0418 CaSO<sub>4</sub>. H_2O = 7.8; Ca = 16.9.
```

$$(C_4H_9O_2)_2Ca + H_2O$$
 requires $H_2O = 7.7$. $Ca = 17.2$ per cent.

The valeric acid in the fraction 180—195° was separated as the valeranilide which melted at 60° (uncorr.), and on analysis gave the following results.

```
0.0660 gave 0.1795 CO_2 and 0.0515 H_2O. C = 74.2; H = 8.7. 0.1998 ,, 13.6 c.c. moist nitrogen at 20.5° and 757 mm. N = 7.8. C_{11}H_{15}NO requires C = 74.6; H = 8.5; N = 7.9 per cent.
```

As the anilide of normal valeric acid has not been described, it was prepared from a sample of normal valeric acid boiling at 185—186°, and was found to melt at 61° (uncorr.). Admixture of the anilide obtained from the fraction 180—195° with the anilide from normal valeric acid did not depress the melting point of the latter. The acid in this fraction is, therefore, normal valeric acid.

The fraction boiling above 195° was converted into the anilide which, after many crystallisations from light petroleum, melted at 93° (uncorr.). The analytical numbers were slightly low for a caproanilide, and lack of material prevented further purification. Normal caproanilide melts at 95°, and since it has been shown that the lower acids belong to the normal series, it can hardly be doubted that the acid obtained from this fraction is normal caproic acid.

In a similar examination of a much larger quantity of the fatty

acids obtained by oxidation of crude cannabinol with nitric acid, the same acids were obtained. Normal butyric acid was identified by its calcium salt, normal valeric acid by its anilide, and caproic acid by its silver salt.

The fraction 150—170° was also examined for isobutyric acid (b. p. 155°) by the method used by V. Meyer and Hutzler (*Ber.*, 1897, 2519), but as no trace of acetonic acid could be detected after oxidadation with potassium permanganate, isobutyric acid is evidently absent.

Caproic acid was also found in the product of the oxidation of crude cannabinol by chromic acid mixture, and by potassium permanganate solution.

In each case, the silver salt was recrystallised until the analytical results were constant. A. From chromic acid mixture oxidation. B. From potassium permanganate oxidation. C. From nitric acid oxidation.

Nitrocannabino-lactone (oxycannabin),

$$C_{11}H_{11}NO_4\cdot NO_2\cdot C_6H_8(CH_8) \stackrel{C_9H_5}{\bigcirc} CO$$
 (3).

The preparation of this substance from trinitrocannabinol has already been described; it can be obtained more conveniently by the following Crude cannabinol is dissolved in three times its weight of glacial acetic acid, warmed to 100°, and nitric acid (sp. gr. 1.42) slowly dropped in from a burette in the proportion of 1 c.c. of nitric acid for each gram of cannabinol; the solution is then boiled gently for half an hour, more nitric acid is added, and the boiling continued for 8-10 hours, nitric acid being added whenever the oxidation slackens, 50 grams of crude cannabinol require in all 300-400 c.c. of nitric acid. The product is then poured into water, and the nitrocannabinolactone separated as before; the yield is 15-20 per cent. of the crude cannabinol used. When purified by repeated crystallisation from alcohol, it is obtained in very faintly yellowish needles melting at 178° (uncorr.), and is not changed by sublimation. On exposure to light, it gradually assumes a reddish tinge. It is soluble in alcohol, acetic acid, benzene, and concentrated nitric acid. These properties show that it is identical with the oxycannabin of Bolas and Francis (loc. cit.), and of Dunstan and Henry (loc. cit.). Five samples were

analysed. A. Purified by sublimation. B. Precipitated from the potassium salt. C. Crystallised from dilute acetic acid. D. From alcohol. E. From trinitrocannabinol, and crystallised from alcohol.

```
0.1478 gave 0.3225 CO<sub>2</sub> and 0.0663 H<sub>2</sub>O. C = 59.5; H = 5.0.
      A.
                                                            0.0580 \text{ H}_{\circ}O. C = 59.2 \text{ ; H} = 4.9.
                                 0.2852 CO. "
      В.
             0.1313
                                                            0.0582 \text{ H}_{\odot}O. C = 59.7; H = 5.4.
             0.1195
                                 0.2615 CO. "
      D. \begin{cases} 0.1330 & \text{,,} & 0.2900 \text{ GO}_2 & \text{,,} & 0.0605 \text{ H}_2\text{O}. \text{ C} = 59.5 \text{; } \text{H} = 5.1. \\ 0.1615 & \text{,,} & 8.8 \text{ c.c. moist nitrogen at } 21^\circ \text{ and } 772 \text{ mm. N} = 6.3. \end{cases}
                                                                        17^{\circ} , 764 , N = 6.6.
                                 8.0
                                                                        19° , 750 , N = 6.4.
             0.1155
                                 6.5
      E.
                                                 requires C = 59.7; H = 5.0; N = 6.3 per cent.
C,H,NO
C<sub>90</sub>H<sub>90</sub>N<sub>2</sub>O<sub>7</sub> (Bolas and Francis)
                                                             C = 60.0; H = 5.0; N = 7.0
                                                              C = 57.7; H = 4.8; N = 6.7
C_{10}H_{10}NO_4(Dunstan and Henry)
```

The molecular weight was determined by the freezing point method in glacial acetic acid.

0.4313 gram, dissolved in 20 grams glacial acetic acid, lowered the freezing point 0.375° .

Mol. wt. calc. for
$$C_{11}H_{11}NO_4 = 221$$
. Found = 225.

Nitrocannabino-lactone is insoluble in cold aqueous alkalis, but dissolves on boiling for a few minutes, and is not precipitated on dilution with water; the addition of mineral acids, however, precipitates it unchanged. Its salts are prepared as follows.

Potassium salt.—This salt separates in slender, pale yellow needles on mixing saturated solutions, in absolute alcohol, of the lactone and caustic potash.

0.1197 gave 0.0375
$$K_2SO_4$$
. $K = 14.1$.
 $C_{11}H_{12}NO_5K$ requires $K = 14.0$ per cent.

Silver salt.—Prepared by adding silver nitrate to an aqueous solution of the potassium salt.

0.1322 gave 0.0409 Ag. Ag = 30.9.

$$C_{11}H_{12}NO_5Ag$$
 requires Ag = 31.3 per cent.

An attempt was made to obtain the ethylic salt by boiling the ailver salt with ethylic iodide; silver iodide separated, but on extracting the product with boiling alcohol, nothing but unaltered nitrocannabino-lactone was obtained.

The lactone was treated with aqueous ammonia, sp. gr. 0.88, and with saturated alcoholic ammonia, both at the ordinary temperature, and in sealed tubes at 100°. In each case, nothing but the unaltered lactone could be recovered. Failing to obtain an amide, an attempt was made to prepare the anilide, but this also was unsuccessful.

Oxidation of Nitrocannabino-lactone with dilute Nitric Acid.—Nitrocannabino-lactone (4 grams) was heated with 25 per cent. nitric acid (80 c.c.) at 185° for 8 hours, and the liquid, on stirring, deposited a colourless, crystalline, sparingly soluble acid; this, after recrystallisation from hot water, melted at 229—230° (uncorr.). The weight of the recrystallised acid was 1·1 grams.

Analysis shows that the substance has the formula $C_{11}H_9NO_6$, which may be derived from nitrocannabino-lactone by the oxidation of a methyl group to a carboxyl group, thus

$$COOH \cdot C_6H_3(NO_2) < C_9H_5 > CO.$$

This conclusion is strengthened by the fact that nitrocannabinolactone, on oxidation with potassium permanganate in the cold, yields the same product. A. Was prepared by oxidation with nitric acid. B. With potassium permanganate.

A.
$$\begin{cases} 0.1053 \text{ gave } 0.0360 \text{ H}_2\text{O and } 0.2033 \text{ CO}_2. & C = 52.7 \text{ ; } H = 3.8. \\ 0.1328 \text{ ,, } 6.5 \text{ c.c. moist nitrogen at } 21^\circ \text{ and } 750 \text{ mm. } N = 5.5. \end{cases}$$

B.
$$\begin{cases} 0.1725 \text{ gave } 0.0612 \text{ H}_2\text{O and } 0.3300 \text{ CO}_2. & C = 52.2 \text{ ; } H = 3.9. \\ 0.1700 & \text{,,} & 8.0 \text{ c.c. moist nitrogen at } 20^\circ \text{ and } 765 \text{ mm.} & N = 5.4. \\ C_{11}H_9NO_6 \text{ requires } C = 52.6 \text{ ; } H = 3.6 \text{ ; } N = 5.5 \text{ per cent.} \end{cases}$$

The acid, neutralised with ammonia, was converted into silver salt. 0.1568 gave 0.0472 Ag. Ag = 30.1.

$$C_{11}H_8NO_6Ag$$
 requires $Ag = 30.2$ per cent.

This acid must be regarded as the nitro-derivative of the cannabinolactonic acid described below.

The nitric acid mother liquor, from which the sparingly soluble acid had separated, was evaporated to dryness, the residue dissolved in a very small quantity of cold water, filtered, again evaporated to dryness and extracted with ether. The syrup left on evaporating the ether gradually deposited crystals which were excessively soluble in water, alcohol, ether, glacial acetic acid, and ethylic acetate, but practically insoluble in benzene, chloroform, and light petroleum. The compound is most satisfactorily purified by recrystallisation from strong hydrochloric acid, when it is obtained as a colourless, crystalline powder, melting at 228—230° with much effervescence, but only a slight discoloration.

Three preparations were analysed.

I. 0-0948 gave 0-0188 H_2O and 0-1478 CO_2 . C = 42.5; H = 2.2. 0-0760 , 3.5 c.c. nitrogen at 20° and 760 mm. N = 5.5.

II. 0.1646 ,, 0.0302 H_2O and 0.2552 CO_2 . C = 42.3; H = 2.0.

III. 0·1775 , 0·0325 H_2O , 0·2754 CO_2 . C = 42·3; H = 2·0. The formula $C_0H_5NO_2$ requires C = 42·3; H = 2·0; N = 5·5.

The acid is tribasic, for on titration with N/10 soda and phenol-phthalein, 0.065 gram required 7.5 c.c. for neutralisation. A tribasic acid of the above formula requires 7.65 c.c.

A solution of the calcium salt of the acid was prepared by neutralisation with chalk, and from this, nitrate of silver precipitated the silver salt as a primrose-yellow powder, slightly soluble in hot water. The salt is feebly explosive.

0.113 gave 0.004 H_2O and 0.079 CO_2 . C = 19.0; H = 0.4. 0.1565 , 0.1172 AgCl. Ag = 56.4. $C_0H_2NO_8Ag_8$ requires C = 18.7; H = 0.3; Ag = 56.2.

No attempt has been made to elucidate the constitution of the acid; it is, however, difficult to account for the formation of a tribasic acid of the formula $C_9H_5NO_8$ from nitrotolylbutyrolactone unless the acid is a hydroxyglyoxylic acid of the constitution

COOH·C,H,(OH)(NO,)·CO·COOH.

Amidocannabino-lactone, $C_{11}H_{11}NH_2\cdot O_2$.—This compound can be obtained by the reduction of the nitrolactone by tin and hydrochloric acid, or by hydriodic acid and phosphorus, but the latter is more convenient.

Ten grams of the nitrolactone dissolved in 40 c.c. of glacial acetic acid was boiled with 30 c.c. of hydriodic acid of sp. gr. 1.6 and 5 grams of phosphorus for 2 or 3 hours, the colourless solution on cooling depositing crystals of the hydriodide of the base, and a further quantity of the base was obtained by pouring the strongly acid mother liquor into water. On dissolving the hydriodide thus obtained in boiling water, dissociation occurs, and the free base crystallises out on cooling.

Amidocannabino-lactone crystallises readily from hot water in long, white needles melting at 119° (uncorr.). Two preparations were analysed. A. Prepared by hydriodic acid and phosphorus. B. By tin and hydrochloric acid.

A. $\begin{cases} 0.1260 \text{ gave } 0.3200 \text{ CO}_2 \text{ and } 0.0770 \text{ H}_2\text{O}. & C = 69.3 \text{ ; } \mathbf{H} = 6.8. \\ 0.1140 & \text{,,} & 0.2895 \text{ CO}_2 & \text{,,} & 0.0720 \text{ H}_2\text{O}. & C = 69.2 \text{ ; } \mathbf{H} = 7.0. \\ 0.1826 & \text{,,} & 11.5 \text{ c.c. moist nitrogen at } 22^\circ \text{ and } 770 \text{ mm. } \mathbf{N} = 7.2. \end{cases}$

B. 0.0795 ,, 0.2005 CO₂ and 0.0500 H₂O. C=68.8; H=7.0. C₁₁H₁₈NO₂ requires C=69.1; H=6.8; N=7.3 per cent.

The hydriodide was also analysed.

0.1957 gave 0.1420 AgI. I = 39.2. $C_{11}H_{11}O_{2}\cdot NH_{21}HI$ requires I = 39.8 per cent.

The platinochloride was prepared by dissolving the base in strong hydrochloric acid and adding platinic chloride solution. Two specimens were analysed.

0.1200 gave 0.0296 Pt. Pt = 24.7. 0.2594 , 0.0636 Pt. Pt = 24.5.

 $(C_{11}H_{11}O_2 \cdot NH_2)_2 H_2 PtCl_6$ requires Pt = 24.6 per cent.

The base was readily diazotised, and an attempt was made to prepare cannabino-lactone from it by Friedländer's method, but no satisfactory product could be obtained.

Cannabino-lactone was, however, easily obtained through the iodolactone, whose preparation is given below.

lodocamabino-lactone, CH₃·C₆H₈I C₅H₅ CO.—Ten grams of amidocamabino-lactone was dissolved in 25 c.c. strong hydrochloric acid, 75 c.c. water added, and the solution diazotised by the addition of 45 grams of sodium nitrite dissolved in 15 c.c. of water, the temperature being kept within a few degrees of the freezing point. 12·5 grams of potassium iodide in 25 c.c. water was then added, and the mixture heated on the water bath until evolution of nitrogen ceased; the acid liquor was then poured off, and the solid residue, after treatment with solution of sodium thiosulphate to remove free iodine, was repeatedly crystallised from dilute acetic acid. The yield was 10 grams. The iodolactone forms almost colourless crystals melting at 137·5° (uncorr.), insoluble in water, but easily soluble in alcohol and acetic acid; it sublimes very readily.

0.2370 gave 0.3825 CO_2 and 0.0803 H_2O . C=44.0; H=3.8. 0.2785 , 0.2145 AgI. I=41.6.

 $C_{11}H_{11}IO_2$ requires C = 43.7; H = 3.6; I = 42.0 per cent.

Silver Salt.—A solution of the potassium salt was obtained by saturating alcoholic caustic potash solution with the iodolactone, and after precipitating the excess of lactone by water, silver nitrate was added to the filtrate. The silver salt was precipitated as an amorphous powder which became crystalline on standing. It is soluble in hot water, but cannot be recrystallised without decomposition.

0.2430 gave 0.1315 AgI. Ag = 24.9 $C_{12}H_{12}IO_{2}Ag$ requires Ag = 25.3 per cent.

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Cannabino-lactons, $CH_3 \cdot C_6H_4 < C_0^8H_5 > CO$.—The iodolactone is dissolved in hot alcoholic potash solution and the solution, diluted with water, is reduced with 2.5 per cent. sodium amalgam. No hydrogen is evolved until almost the theoretical amount of amalgam has been added, but it is found advantageous to use a considerable excess of the reducing agent in order to ensure the complete removal of iodine. After the alcohol has been removed by boiling, the alkaline solution is acidified

by sulphuric acid, and steam distilled until the distillate no longer becomes turbid on adding a strong solution of potassium carbonate. The lactone is obtained by salting out the distillate with potassium carbonate, and extracting with ether; the oily residue left on evaporating the ether distilled almost to the last drop at 290.5° (uncorr.) under a pressure of 768 mm. When purified by redistillation under diminished pressure, it was obtained as a colourless, highly refracting liquid of sp. gr. at $20^{\circ}/20^{\circ} = 1.0833$, and boiling at 126° (uncorr.) (20 mm.). The yield of pure cannabino-lactone from the iodolactone amounts to 86 per cent. of the theoretical.

0.1105 gave 0.3055 CO₂ and 0.0700 H₂O.
$$C = 74.9$$
; $H = 7.0$. $C_{11}H_{12}O_2$ requires $C = 75.0$; $H = 6.8$ per cent.

The lactone dissolves slowly in aqueous solution of caustic alkalis, and is reprecipitated by carbon dioxide. So great is the tendency to lactone formation that a current of steam slowly removes the lactone from its solution in excess of caustic potash.

Cannabino-lactonic Acid, COOH·C₆H₄C₈H₅CO.—11·5 grams of cannabino-lactone, dissolved in hot aqueous potash, was treated with 41·4 grams of potassium permanganate dissolved in 1000 c.c. of water, and the mixture, after being boiled for 9 hours, was decolorised by a few drops of alcohol. The filtrate from the manganese dioxide, when evaporated to 200 c.c. and acidified with hydrochloric acid, deposited 10·6 grams of a pearly-white, crystalline compound, which, after recrystallisation from hot water, was obtained in long needles melting at 203° (uncorr.). The yield is 88 per cent. of the theoretical. Two samples were analysed.

The lactonic acid is soluble in about 85 parts of boiling water, very sparingly in cold water, and easily in alcohol.

Potassium Salt.—Prepared by adding alcoholic potash to an alcoholic solution of the lactonic acid.

0.2295 gave 0.0825
$$K_2SO_4$$
. $K = 16.1$. $C_{11}H_2O_4K$ requires $K = 16.0$ per cent.

The silver salt was found to contain 33.8 per cent. Ag. $C_{11}H_9O_4Ag$ requires 34.5 per cent.

The *ethylic salt* was prepared by boiling the lactonic acid for 5 hours with a 3 per cent. solution of hydrogen chloride in absolute alcohol. After recrystallisation from dilute alcohol, it melted at 105° (uncorr.), and, on analysis, gave the following numbers.

0.0861 gave 0.2095 CO_2 and 0.0484 H_2O . C=66.4; H=6.2. 0.1608 , 0.3905 CO_2 , 0.0890 H_2O . C=66.2; H=6.1. $C_{11}H_9O_4 \cdot C_2H_5$ requires C=66.7; H=6.0 per cent.

Fusion of Cannabino-lactonic Acid with Potash.

4.4 grams of the lactonic acid was fused with 25 grams moist caustic potash at 286° (in a bath of boiling β -naphthol). The reaction is completed almost instantaneously at this temperature, but proceeds with extreme slowness at 220°. The melt, on being dissolved and acidified with dilute sulphuric acid, gave 3.4 grams of a crystalline precipitate, which, after several recrystallisations from dilute alcohol, sublimation, and a further recrystallisation, melted above 300°, and sublimed without decomposition.

0.1133 gave 0.2392 CO₂ and 0.0400 H₂O. C = 57.6; H = 3.9. $C_8H_6O_4$ requires C = 57.8; H = 3.6 per cent.

The analysis and physical characters agree with those of isophthalic acid.

Its methylic salt melted at 64° (uncorr.), and boiled at 280—282° (uncorr.) (Baeyer gives 64—65°, Annalen, 1873, 166, 340). The salt, on analysis, gave the following numbers.

0.1084 gave 0.2445 CO₂ and 0.0518 H₂O. C = 61.5; H = 5.3. 0.1060 , 0.2395 CO₂ , 0.0510 H₂O. C = 61.7; H = 5.3. $C_6H_4(COOCH_3)_2$ requires C = 61.9; H = 5.1 per cent.

Potash Fusion of Cannabino-lactone with Potash.

The conclusions to be drawn from the fusion of cannabino-lactonic acid are supported by the potash fusion of cannabino-lactone (0.9 gram) with moist caustic potash (15 grams) at 300° to 320°, which yields metatoluic acid.

The reaction took place slowly, and the melt, which was very dark in colour, was dissolved, acidified with sulphuric acid, and extracted with ether, &c., in the usual way. After purifying the product by crystallisation from water and animal charcoal 0·3 gram was obtained. It began to melt at 108°, but was not completely melted until 200°. It was accordingly steam distilled, and the crystals, which separated in the distillate, were now found to melt at 110° (uncorr.). Jacobsen (Ber., 1881, 14, 2349) gives the melting point of metatoluic acid as 110·5°. The mother liquor from which the metatoluic acid had been removed by steam distillation, on being evaporated to dryness, dried at 150°, and then recrystallised from water, gave isophthalic acid, which melted above 300°, and sublimed without decomposition; this was, no doubt, produced from the metatoluic acid by further oxidation.

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Reduction of Cannabino-lactonic Acid.

The lactonic acid was reduced by heating with hydriodic acid and phosphorus in a sealed tube at 190°, and the product, after two recrystallisations, melted at about 210°. As the limited quantity of the substance did not allow of further purification, it was analysed. The result leaves no doubt that it is the expected metacarboxy-phenylbutyric acid.

(1) $COOH \cdot C_6H_4 \cdot C_8H_6 \cdot COOH$ (3).

0.1298 gave 0.3044 CO_2 and 0.0695 H_2O . C=64.0; H=5.9. $C_{11}H_{12}O_4$ requires C=63.5; H=5.8 per cent.

University Chemical Laboratory, Cambridge.

IV.—Characterisation of Racemic Compounds.

By FREDERIC STANLEY KIPPING and WILLIAM JACKSON POPE.

We have previously shown (Trans., 1897, 71, 989) that the results of the study of a number of externally compensated substances indicate that only one method is at present of really practical use for characterising solid racemic compounds, that, namely, which is based on the determination of the crystalline forms of the optically active and externally compensated materials; and, in accordance with this conclusion, we defined crystalline racemic and pseudoracemic compounds from a purely crystallographic standpoint (loc. cit., 993). But the crystallographic constants of an organic substance are not always determinable with ease and completeness; hence the establishment of other criteria of racemism is a matter of considerable importance.

Now, Liebisch has shown (Annalen, 1895, 286, 140) that a comparison of the densities of the optically active and externally compensated compounds affords a very simple method for the determination of racemism (compare Walden, Ber., 1896, 29, 1692); unfortunately, however, the results of the experimental determination of a difference between two density constants, especially when this difference is very small, as it frequently may be, can hardly be considered so conclusive as those derived from the much more complex series of constants constituting the crystallographic properties.

This difficulty of ascertaining, except by crystallographic determinations, whether certain substances are really racemic on the one hand, or merely pseudorscemic or externally compensated mixtures on

the other, has led to attempts being made to devise simpler methods for the determination of racemism. Thus, Ladenburg (Ber., 1894, 27, 3065) formulates "eine allgemeine Methode, um Gemenge enantiomorpher Körper von racemischen Verbindungen zu unterscheiden. Sobald es gelingt, die in Frage stehende Substanz, die wenigstens einen kleinen Ueberschuss der einen drehenden Modification enthalten muss, durch Behandlung mit inactiven Körpern in Fractionen von verändertem Drehungsvermögen zu verwandeln, liegt stets eine Verbindung vor."

Now this method, if really applicable, should prove of great value, but inasmuch as Ladenburg adduces no experimental evidence supporting its validity as a means of discrimination, but uses it without further inquiry in order to decide as to the racemic nature of externally compensated coniine, the conclusions based on its use cannot be regarded as in any way decisive.

Moreover, the method is arrived at by means of a curiously fallacious piece of reasoning, for, just before the above quotation, Ladenburg writes: "es ist, wie ich glaube, eine bisher ausnahmlos bestätigte Thatsache, dass enantiomorphe Körper stets die gleiche Löslichkeit besitzen und daher auch in Verbindung mit inactiven Stoffen nicht durch Krystallisation oder partielle Fällung getrennt werden können."

Now there seems not the least justification, experimental or theoretical, for the deduction which Ladenburg draws from the fact of the equal solubility of the two enantiomorphously related substances, namely, that a mixture of unequal quantities could not be separated by crystallisation or partial precipitation. There is, in fact, no evidence that an inactive non-racemic mixture has the same solubility as either of its active components and if its solubility be greater, then, on concentrating a solution containing such a nonracemic mixture together with excess of one enantiomorph, at constant temperature, that excess would crystallise first, leaving material of lower specific rotation in solution; a continuation of this process would ultimately afford a mother liquor containing an inactive non-racemic mixture. The solution would then go on depositing dextro- and levomaterial in equal proportion as evaporation proceeded, casual disturbances of equilibrium such as always occur in a crystallising solution being, of course, disregarded. Obviously, therefore, any arguments based upon our present knowledge of the laws governing solubility should have led Ladenburg to a conclusion diametrically opposed to that at which he actually arrived.

The question of the racemic nature of externally compensated conine has lately been again considered, and Küster (Ber., 1898, 31, 1847), arguing from the solubility products of the various isomerides, con-

cludes that a large part of the inactive substance exists in solution in a racemic condition. Although this conclusion may be true, yet, inasmuch as no case has been investigated in which the solubility values indicate that no racemism occurs in the solution, or in the solid state, as the case may be, Küster's method cannot be accepted. A hypothesis founded upon one set of phenomena often gives valuable indications as to the direction in which work should be done in connection with the examination of a second set of phenomena, but these are merely indications, and require experimental verification before the hypothesis can be extended so as to cover the new ground. The cases dealt with by Küster are instances in which the ordinary solubility laws applying to two mutually inactive solutes are not followed; when a case is found amongst externally compensated substances in which the solubility determinations indicate the non-existence of a racemic compound in solution, Küster's method will become of practical value. Until then, however, it must be classed with Ladenburg's method as an untried one.

In order to ascertain the accuracy or otherwise of Ladenburg's argument, we have examined three cases experimentally; those, namely, of sodium ammonium tartrate, sodium potassium tartrate, and potassium hydrogen tartrate.

Sodium Ammonium Dextro- and Lavo-tartrates.

An externally compensated mixture of dextro- and lævo-sodium ammonium tartrates is known to be non-racemic at ordinary temperatures, but becomes racemic at and above 27° (van't Hoff and Deventer, *Ber.*, 1886, 19, 2148); below this temperature, the salt separates from solution as a mere mixture of the two tartrates.

Now, if Ladenburg's rule be applicable, on crystallising the sodium ammonium salt of racemic acid with an excess of sodium ammonium dextrotartrate below 27°, the successive fractions should have the same specific rotation; but, as a matter of fact, the behaviour of the mixture on crystallisation is that which would be expected from our interpretation of the laws governing the equilibrium of such solutions.

In a preliminary experiment, an intimate mixture of 25 grams of sodium ammonium dextrotartrate with 5 grams of the corresponding is evotartrate was made; it was found to have the specific rotation $[a]_D = +15.60^\circ$ in a 5 per cent. solution, instead of the calculated value $[a] = +15.76^\circ$. The mixture was dissolved in cold water and set aside to evaporate; after several days, a fraction (1) separated and was collected, washed with cold water, and dried in the air. The mother liquor and washings were mixed and set aside to crystallise.

when a further separation (2) was obtained; this was removed as before, the mother liquors evaporated to dryness, and the residue collected. During the experiment, the laboratory temperature never rose above 15°; the weights and rotations of these fractions were as follows.

		Weight.	[a] _D
Total mat	erial	30 g.	+15.60°
First fraction,	(1)	8 g,	+23.51
Second ,,	(2)	13 g.	+20.27
Third "	(3)	8 g.	0

Instead of all the three separations having the same specific rotation as the original mixture, as required by Ladenburg's rule, the first two fractions consisted almost entirely of dextrotartrate, whilst a 5 per cent. aqueous solution of the residue in the mother liquor had no observable rotation in a 200 mm. tube.

In order to trace this process of separation more carefully, and thus obtain further data, the following experiments were made. A mixture of 26·1 grams of sodium ammonium dextrotartrate, with an equal weight of the salt obtained from racemic acid, was made; this mixture, having a specific rotation of $[a]_{\rm b}=+11\cdot82^{\circ}$, was dissolved in water and allowed to crystallise spontaneously at the ordinary laboratory temperature, which never rose above 18°, namely, 9° below the temperature at which a racemic compound begins to separate. As the various deposits were obtained, they were separated by means of the filter pump (but not washed free from mother liquor) and examined, the fractionation proceeding in accordance with the following scheme (next page).

The weights, w, and the specific rotations a, of the various fractions are given in columns 2 and 3 respectively of Table I (p. 41), columns 5 and 6 give respectively the excess of dextro-over inactive salt in 100 parts of the various fractions, and the actual weights in grams of the excess of dextro-salt in these fractions.

The weight of salt recovered from the $52\cdot2$ grams dissolved was $\Sigma w = 51\cdot25$ grams; the weighted mean specific rotation of all the fractions is $\Sigma wa/\Sigma w = +12\cdot20^\circ$, and if the weight of salt taken, namely, $52\cdot2$ grams be substituted for Σw , the mean specific rotation $\Sigma wa/52\cdot2 = +11\cdot98^\circ$ is obtained.

The mixture of salts actually had the specific rotation $[a]_D = +11.82^\circ$ so that within the limits of the experimental errors unavoidably incurred in so long a series of fractionations, the whole of the salt used is accounted for.

The specific rotation of sodium ammonium dextrotartrate,

 $Na(NH_4)C_4H_4O_6 + 4H_2O_5$

is [a]_D = +23.64°, and the first large deposit of 32.1 grams contained

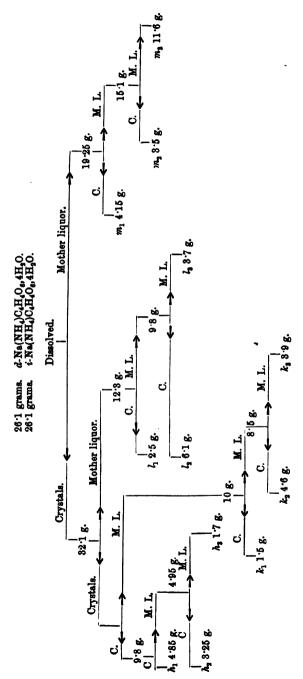


TABLE I.

1.	2.	3.	4.	5.	6.
Fraction.	w. grams.	æ.	10a.	Percentage excess of d-salt.	Weight of excess of d-salt. D.
Å ₁ Å ₂ Å ₃	4 85	+ 23·23	+112.67	+ 98 · 26	+4.766
	8 25	+ 23·23	+75.50	+ 98 · 26	+8.194
	1 70	+ 21·55	+86.64	+ 90 · 36	+1.550
k ₁	1:50	+ 23·47	+35-20	+99·28	+1.488
k ₂	4:60	+ 28·12	+106-85	+97·80	+4.499
k ₃	8:9	+ 23·02	+89-78	+97·38	+8.798
i, i,	2·5 6·1 8·7	+22.51 +10.51 0	+56-27 +64-11 0	+95·22 +46·46 0	+2:881 +2:712 0
m ₁	4·15	+15.52	+64·41	+65°65	+2.724
m ₃	8·5	-22.40	-78·40	-94°75	-8.816
m ₃	11·6	+5.41	+62·76	+22°88	+2.655

2w = 51.25.

210a = +625.29.

3D = +26.451.

$$\frac{260a}{360} = +12.20^{\circ}$$
.

$$\frac{3wa}{52.2} = +11.98^{\circ}$$

28.25 grams of sodium ammonium dextrotartrate and 3.85 grams of the isomeric lavo-salt; this corresponds with 24.4 grams of the sodium ammonium dextrotartrate with 7.7 grams of the inactive mixture, so that nearly the whole of the 26.1 grams of the dextro-salt originally taken was deposited in the first crop of crystals. After the next separation, m, from the mother liquor, 27.1 grams of the dextrotartrate had separated in addition to inactive material; consequently, the mother liquor was strongly levorotatory, and the next separation, m_2 , was a levorotatory one. Practically, all the excess of the dextrorotatory salt was contained in the first fractions, $h_1, h_2, h_3, k_1, k_2, k_3$, and I, which consisted almost entirely of this salt, but still contained small quantities of the inactive material, partly because the crystals were not washed, and partly, no doubt, because of occluded mother liquor, which is often present in noticeable quantity. The further changes during crystallisation will be understood from the tabulated resulta.

In a recent paper (Trans., 1897, 71, 999), we have shown that externally compensated camphorsulphonic chloride (Trans., 1893,68, 560) and camphorsulphonic bromide (Trans., 1895, 67, 359) are probably pseudoracemic; consequently, they behave, on crystallisation, like non-

racemic compounds and the ethylic acetate solutions of a strongly dextrorotatory mixture of the sulphonic chlorides deposits, on evaporation, part, or the whole, of the excess of the dextro-compound; after the solution has thus become nearly or quite inactive, further crystallisation affords deposits which sometimes contain an excess of one or other isomeride, a behaviour which is obviously very similar to that of the sodium ammonium tartrates.

Sodium Potassium Dextrotartrate and Racemate.

Having shown by the foregoing experiments that Ladenburg's method does not hold in the case of non-racemic sodium ammonium dextro- and lawo-tartrates, namely, in the only test case on which the method has yet been worked out, we thought it advisable to apply the same method to a case in which a crystalline racemic compound undoubtedly exists, in order to ascertain whether the fractional separation occurs in a manner essentially different from that observed in the case of a non-racemic mixture.

Sodium potassium dextrotartrate is isomorphous with the corresponding sodium ammonium salt and, at temperatures between -6° and $+41^{\circ}$, forms a racemic compound with the isomeric levotartrate (van't Hoff and Deventer, *Zeit. physik. Chem.*, 1895, 17, 505); it therefore forms a racemic compound at ordinary temperatures. The optically active substances have the composition NaKC₄H₄O₆ + 4H₂O, whilst the composition of the racemate is NaKC₄H₄O₆ + 3H₂O.

A mixture of 47.4 grams of sodium potassium dextrotartrate with 44.4 grams of the racemate (molecular proportions) was dissolved in water and fractionally crystallised as before; the scheme given on the next page shows how the various fractions were collected. Table II (p. 44) gives the weights, w, and the specific rotations, a, for the D-line; columns 5 and 6 give the values corresponding with those in Table I.

The specific rotation of the anhydrous dextrotartrate, KNaC₄H₄O₆, is $[a]_D = +29.67^\circ$ (Landolt); that of the mixture of 47.4 grams of hydrated dextrotartrate with 44.4 grams of the racemic salt is, therefore, $[a]_D = +11.41^\circ$. The weighted mean specific rotation of all the separated fractions is

$$[a]_D = \frac{\sum wa}{\sum va} = +11.34^\circ,$$

whilst

$$\frac{\sum wa}{91.8} = +11.28^{\circ}.$$

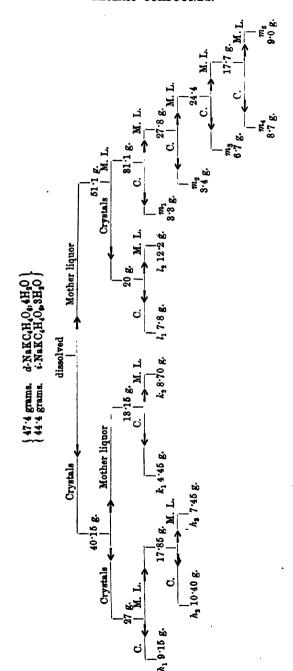


TABLE II.

1	2.	8.	4.	5.	6.
Fraction.	w. grams.	a.	wa.	Percentage excess of d-salt.	Weight of excess of d-salt. D.
h,	9.15	+22·08°	+202.0	+ 99 - 78	+9.125
h.	10.40	+21.77	+ 226 6	+ 98.88	+10.230
h ₁ h ₂ h ₃	7.45	+21.56	+160.6	+97.38	+7-255
k 1	4.45	+21.25	+94.6	+95.98	+4.271
k ₁ k ₂	8.70	+ 17 .20	+152.2	+79.22	+6.891
l ₁	7.8	+ 21 .85	+166.5	+ 96.48	+7.528
l ₁	12-2	+4.58	+ 55 9	+81.90	+8.364
m ₁	8.8	- 20:00	- 66.0	- 90 84	- 2.981
m_2	3·4	+10.00	+84.0	+45.17	+1.536
m ₃	6.7	+1.35	+9.0	+6.10	+1.408
m_4	8·7	0 .	0	0	0
m_5	8.0	0	0	0	0

$$\exists w = 91.25.$$
 $\exists w\alpha = +1085.4.$ $\exists D = +47.622$ $\exists D = 58.584.$ $\frac{\exists w\alpha}{\exists 1.9} = +11.28^{\circ}.$

The agreement between the quantities and specific rotations of the material taken, and the quantities and specific rotations of the fractions recovered, is hence highly satisfactory.

From an inspection of Table II, it is seen that the successive fractions separating from the solution decrease in specific rotation, that is to say, they contain decreasing quantities of the dextrotartrate in excess of the racemate, and ultimately the mother liquors contain nothing but pure racemate. The table also shows the following curious facts: the fractions h, k, and l contain 48.66 grams of the dextrotartrate as such, whilst material corresponding with only 47.4 grams was used; the difference of 1.26 grams, therefore, must be ascribed either to experimental error or to the fact that part of the racemate used was resolved, and the dextrorotatory component deposited here. That the latter alternative is the true one is shown by the mother liquor becoming lævorotatory. Consequently, on crystallising the latter, the first deposit, m,, is strongly lavorotatory, containing 90.34 grams of levotartrate to each 9.66 grams of racemate; 2.98 grams of levotartrate crystallised as such in m_1 , whilst the solution only contained 1.26 grams excess of this salt. In the end, therefore, 50.38 (47.4 + 2.98) grams of dextrotartrate had separated

from solution as such, or about 3 grams more than had been used; it follows, therefore, that a partial resolution of the racemate had occurred, about 6 grams being so resolved. The good agreement of the sums of the weights of salt separated from the solution and the mean rotation of the fractions, on the one hand, with the weight of salt and the mean specific rotation which should have been obtained, on the other hand, is proof that we are not here being misled by experimental error.

The interesting work of Purdie on the resolution of lactic acid into its optically active components (Trans., 1893, 63, 1143) affords a case, similar to the above, of the resolution of a racemic compound. Racemic zinc ammonium lactate crystallises with $3\rm{H}_2\rm{O}$, and when its supersaturated solution is sown with a crystal of either of the optically active isomerides, that particular isomeride separates in crystals containing $2\rm{H}_2\rm{O}$; this resolution is similar to that which has occurred in fractions l_2 and m_1 of our mixture.

We are thus led to the following conclusion: a racemic compound may, under certain conditions, be resolved into its optically active components by simple crystallisation, at temperatures at which the racemic compound is more stable than the mixture of the two optically active salts.

A comparison of Tables I and II shows that the fractional crystallisation has followed much the same course in the case of the racemic compound as in that of the non-racemic mixture; the separation of the racemic compound from the dextrorotatory one is, however, not quite so sharp as in the separation of the non-racemic mixture.

Potassium Hydrogen Dextrotartrate and Racemate, KHC, H,O,.

In the foregoing cases, the inactive mixture or compound is more soluble than either of the active components; it seemed desirable, therefore, to investigate a case in which the contrary is true. Such a case was found on examining the behaviour of the potassium hydrogen tartrates. On crystallising a mixture of equal quantities of the dextrotartrate and of the racemate, by allowing the hot solution to cool, it was found that the mother liquor contained a salt of much higher specific rotation than that of the mixture deposited; by repeatedly recrystallising the deposit, the specific rotation of the material in the successive mother liquors remained nearly constant, and of very much higher value than that of the crystalline separations. Owing to the sparing solubility of these two salts, they had to be dissolved in dilute ammonia for the rotation determinations. The results need not be quoted in full, because they were in so many respects similar to the preceding cases, and the experimental error was greater.

The examination of these three cases shows that Ladenburg's method does not constitute a means of discriminating between cases in which a solid racemic compound is formed, and those in which a mere inactive mixture is obtained; a scrutiny of Tables I and II will show that this method gives practically the same results with a well-defined racemic compound as with a non-racemic mixture.

It may possibly be objected that, although inactive sodium ammonium tartrate does not exist as a solid racemic compound at ordinary temperatures, it may exist as a racemic compound in solution; to make this assumption unsupported by experimental evidence is, however, unjustifiable, and can only be regarded as an expression of opinion.

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V.—Crystalline Form of Iodoform.

By WILLIAM JACKSON POPE.

UP to the present, no geometrical measurements with any pretensions to accuracy have been made on crystals of iodoform, the only available data consisting of two angles measured by Rammelsberg (*Kryst.-physik. Chem.*, 1882, 2, 321); these measurements cannot, however, be credited with much value since Rammelsberg remarks of his crystals that "die Flächen sind ziemlich matt."

Considerable difficulty is found in obtaining well developed crystals of iodoform using the ordinary organic solvents such as alcohol or benzene. Iodoform is, however, fairly soluble in acetone, and on allowing the cold solution to evaporate spontaneously at a uniform temperature, magnificent, transparent, six-sided tablets of iodoform separate; in order to obtain the best results, the acetone should be as free from water as possible. Even when pure, almost odourless iodoform is used, blackening occurs round the sides of the vessel, and some product, probably iodacetone, is formed during the evaporation which excites to tears, and powerfully affects the mucous membrane.

The crystals, which may readily be obtained of a centimetre in diameter, and several millimetres in thickness, are uniformly developed, and the faces give very perfect reflections on measurement. The dominant form is c {111}, the pyramid r {100, 22 $\overline{1}$ } being very much smaller; the prisms p { $\overline{110}$ } and m { $\overline{211}$ } are rarely observed and are always small (see Fig. 1). The crystals are very hard and brittle, free

from striations, and have no noticeable cleavage; they show a six-sided internal growth of hexagonal symmetry when allowed to grow rapidly.

The normal hexagonal optic axial interference figure is seen on conscopic examination through the faces of c {111}; the double refraction is strong and negative in sign.

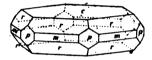
Rammelsberg (loc. cit.) determined the angles cr (111:100) = 52° 0′ and rr (22 $\overline{1}$:100) = 46° 30′, gives the axial ratio $a:c=1:1\cdot108$, and only observed the forms c {111} and r {100, 22 $\overline{1}$ }.

Crystalline system.—Hexagonal.

$$a:c=1:1\cdot1084.$$
 $a=93^{\circ}41'.$

Forms observed
$$c$$
 {111}......{0001} r {100, $22\overline{1}$ }......{10\overline{11}} p {\overline{110}}......{\overline{2110}}{01\overline{10}}

Fig. 1.



The following angular measurements were obtained.

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$\sigma = 111:100$ $\tau = 100:010$ $\tau = 22\overline{1}:00\overline{1}$ $\tau = \overline{1}00:010$ $\tau = \overline{1}10:010$ $\tau = 22\overline{1}:\overline{1}00$ $\tau = 22\overline{1}:\overline{1}00$ $\tau = 111:\overline{1}10$ $\tau = 100:2\overline{1}$	38 16 47 15 22 84 19 13	51°55′— 52° 7′ 85 58 — 86 6 75 50 — 76 6 98 54 — 94 8 46 43 — 47 2 46 20 — 46 25 133 82 — 183 41 89 57 — 90 4 87 54 — 88 9	51°59′50″ 86 2 0 76 0 30 93 58 10 46 57 80 46 23 40 133 36 10 90 0 20 38 2 0	86° 2′20″ 76 0 20 93 57 40 46 58 50 46 24 0 133 36 0 90 0 0 38 0 10

After cautious melting under a cover slip on a microscope slide, iodoform crystallises readily, giving broad, individual crystal flakes, the surfaces of which are parallel to $c\{111\}$; the optic axis of negative double refraction emerges normally to the film surface.

It is interesting to note that a large proportion of compounds of simple constitution crystallise in systems of high symmetry, such as the cubic or hexagonal. It may also be remarked that, whilst the molecule of carbon tetriodide has partial cubic symmetry and crystallises in the cubic system, the molecule of iodoform has partial hexagonal

symmetry and crystallises in the hexagonal system. Many other similar analogies could be quoted, and although complications due to polymorphism frequently occur, it may be stated that a knowledge of the chemical constitutions of simple compounds often allows of a safe prognosis of the crystalline form which those compounds assume.

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VI.—\$\beta\cdot Dimethylglutaric Acid and its Derivatives; Synthesis of cis- and trans-Caronic Acids.

By WILLIAM H. PERKIN, jun., and Jocelyn F. Thorpe.

CABONE, C₁₀H₁₆O, one of the most important ring ketones in the terpene series, is formed when dihydrocarvone hydrobromide is treated with alcoholic potash, hydrogen bromide being eliminated, a decomposition which, according to G. Wagner,* may be formulated in the following manner.

Dihydrocarvone hydrobromide.

Carone.

This view of the constitution of carone was considered probable by Baeyer, who, in order to confirm this formula, carried out a number of important experiments on carone, during the course of which he, in conjunction with Ipatieff, investigated the behaviour of this substance on oxidation with permanganate (Ber., 1896, 29, 2796). It was found that, although carone is very stable towards permanganate at the ordinary temperature, it is moderately readily oxidised at 100°, with formation of two isomeric dibasic acids, $C_5H_8(COOH)_2$, melting at 176° and 212°, which were named caronic acids. The former of these, which is produced in much the larger quantity, readily yielded an anhydride melting at 54—56° when boiled with acetyl chloride, but the other acid was not affected by this treatment.

^{*} Compare Baeyer (Ber., 1896, 29, 5 and 2796).

A careful examination of these acids led Baeyer and Ipatieff to the conclusion that the caronic acids were stereoisomeric modifications of dimethyltrimethylenedicarboxylic acid.

and that these were formed by the oxidation of carone at the points indicated by the dotted lines in the formula

That these acids have the same structure and are stereoisomeric seemed probable from their behaviour towards hydrobromic acid at 100°, under which conditions both are converted into terebic acid with disruption of the trimethylene ring (loc. cit., p. 2801).

$$\begin{array}{c} \text{C(CH}_{3})_{2} & \text{BrC(CH}_{3})_{2} \\ \text{COOH} \cdot \text{CH} \cdot \text{COOH} + \text{HBr} = \text{COOH} \cdot \text{CH}_{2} \cdot \text{CH} \cdot \text{COOH} \\ \text{O} & \text{C(CH}_{3})_{2} \\ = \text{CO} \cdot \text{CH}_{2} \cdot \text{CH} \cdot \text{COOH} \\ \end{array}$$

No mention is, however, made of any attempt to convert the one modification into the other.

In studying this important work, it seemed to us that it would be most interesting to find some means of synthesising the caronic acids, and of thus placing their constitution beyond doubt. This was ultimately accomplished in the way described in this paper.

Some time since, it was shown by Goodwin and Perkin (Trans., 1896, 69, 1475), that ethylic dimethylacrylate condenses with the sodium derivative of ethylic malonate with formation of ethylic dimethylpropanetricarboxylate,

 $(COOC_2H_5)_2CH \cdot C(CH_3)_2 \cdot CH_2 \cdot COOC_2H_5$, and from this, by hydrolysis and elimination of carbon dioxide, $\beta\beta$ -dimethylglutaric acid, $COOH \cdot CH_2 \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH$, was prepared.

The yield of acid obtained in this way is small, but by substi-VOL. LXXV tuting ethylic cyanacetate for ethylic malonate in the condensation with ethylic dimethylacrylate, we now find that the yield of condensation product, which consists of a mixture of some ethylic a-cyano- $\beta\beta$ -dimethylglutarate, COOC₂H₅·CH(CN)·C(CH₃)₂·CH₂·COOC₂H₅, with much of the hydrogen ethylic salt, COOH·CH(CN)·C(CH₃)₂·CH₂·COOC₂H₅, is more than 80 per cent. of the theoretical, and, as these ethereal salts, on boiling with 50 per cent. sulphuric acid, are quantitatively converted into $\beta\beta$ -dimethylglutaric acid, it is now an easy matter to prepare this acid in quantity.

When the anhydride of dimethylglutaric acid is treated with phosphorus pentabromide and bromine, and the product poured into absolute alcohol, ethylic bromodimethylglutarate,

COOC₂H₅·CHBr·C(CH₃)₂·CH₂·COOC₂H₅, is produced, together with large quantities of the hydrogen ethylic salt of the same acid, COOH·CHBr·C(CH₃)₂·CH₂·COOC₂H₅; that the latter should be produced in such quantities is certainly remarkable, and a possible explanation of its formation is given in the experimental part of this paper. When ethylic bromodimethylglutarate is digested with alcoholic potash, hydrolysis and elimination of hydrogen bromide takes place simultaneously, and a mixture of acids is obtained which, by conversion into the ammonium salts and treatment with alcohol, as recommended by Baeyer and Ipatieff (loc. cit., 2978), is easily separated, and found to consist of large quantities of transcaronic acid, some lactone acid of hydroxydimethylglutaric acid (see below), and traces of cis-caronic acid.

This synthesis of the caronic acids may be represented in the following way.

$$C(CH_3)_2$$
 $C(CH_3)_2$ $C(CH_3)_2$ $C(CH_3)_2$ $COOH \cdot CH - CH \cdot COOH$.

Hydrogen ethylic bromodimethylglutarate, COOH·CHBr·C(CH₃)₂·CH₂·COOC₂H₅,

on treatment with alcoholic potash, is quantitatively converted into trans-caronic acid, apparently without even traces of the cis-modification being formed. The synthesis of a trimethylene compound in the manner represented above is remarkable, but a few similar cases have been observed, as, for example, in the formation of acetyltrimethylene by the action of alkalis on acetylpropyl bromide,

$$CH_{3} \cdot CO \cdot CH_{2} \stackrel{CH_{2}}{\leftarrow} CH_{2}Br = CH_{8} \cdot CO \cdot CH \stackrel{CH_{2}}{\leftarrow} CH_{2} + HBr.$$

The synthetical caronic acids have been very carefully investigated, and it is shown in the experimental part of this paper that their pro-

perties agree in all respects with those of the acids obtained by Baeyer and Ipatieff from carone, so that there cannot be any doubt as to the identity of the acids produced by these different methods.

One additional point of interest has been discovered, namely, that trans-caronic acid is converted into the anhydride of cis-caronic acid by the action of acetic anhydride at 220°, a transformation of the trans- into the cis-modification which was required to clearly show that these two acids are stereoisomeric.

Furthermore, it is shown in this paper that aqueous sodium carbonate hydrolyses the hydrogen ethylic salt of bromodimethylglutaric acid, $COOH \cdot CHBr \cdot C(CH_2)_2 \cdot CH_2 \cdot COOO_2H_5$, in a manner quite different from alcoholic potash, with formation of the *lactone* of a-hydroxy- $\beta\beta$ -dimethylglutaric acid, $COOH \cdot C \cdot C(CH_8)_2 \cdot CH_2$, a beautifully crystone $COOH \cdot C \cdot C(CH_8)_2 \cdot CH_2$, a beautifully crystone $COOH \cdot C \cdot C(CH_8)_2 \cdot CH_2$.

talline substance which melts at 112° and is isomeric with the caronic acids.

When ethylic bromodimethylglutarate,

COOC₂H₅·CHBr·C(CH₈)₂·CH₂·COOC₂H₅,

is digested with diethylaniline, hydrogen bromide and ethylic bromide are eliminated and an ethereal salt is obtained, which, on examination, has been found to consist of the ethylic salts of trans-caronic acid, and of the lactons of hydroxydimethylglutaric acid.

EXPERIMENTAL.

Condensation of Ethylic Dimethylacrylate with the Sodium Derivative of Ethylic Cyanacetate.

ββ-Dimethylglutaric acid, COOH·CH₂·C(CH₃)₂·CH₂·COOH, the acid which is the starting-point in the synthesis of the caronic acids, was first prepared by Goodwin and Perkin (Trans., 1896, 69, 1475), who obtained it by the following series of reactions.

Ethylic dimethylacrylate was, in the first place, digested with the sodium derivative of ethylic malonate in alcoholic solution, when condensation took place with formation of ethylic dimethylpropanetricarboxylate,

$$\begin{aligned} (\text{COOC}_2\textbf{H}_5)_2\textbf{CH}_2 + (\text{CH}_3)_2\textbf{C} : \textbf{CH} \cdot \textbf{COOC}_2\textbf{H}_5 = \\ (\text{COOO}_2\textbf{H}_5)_2\textbf{CH} \cdot \textbf{C}(\textbf{CH}_8)_2 \cdot \textbf{CH}_2 \cdot \textbf{COOC}_2\textbf{H}_5. \end{aligned}$$

This ethereal salt, on hydrolysis, yields the corresponding tribasic acid, which, at 200°, loses carbon dioxide with formation of $\beta\beta$ -dimethylglutaric acid, COOH·CH₂·C(CH₃)₂·CH₂·COOH, and from this the anhydride is readily prepared by treatment with acetic anhydride. The yield of the original triethylic salt is unfortunately not good, and

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seldom reaches more than 40 per cent. of the theoretical; indeed, the average yield is scarcely more than 28 per cent. Until quite recently, we have prepared all the dimethylglutaric anhydride required for this research by the method devised by Goodwin and Perkin. A few months since, however, we discovered that the yield may be very greatly improved by substituting ethylic cyanacetate for ethylic malonate in the condensation with ethylic dimethylacrylate, the yield of condensation product being increased to at least 80 per cent. by this means.*

Ethylic a-cyano- $\beta\beta$ -dimethylglutarats,

COOC₂H₅·CH(CN)·C(CH₃)₂·CH₂·COOC₂H₅,

has been prepared in large quantities by the above process, the details of preparation being the following. Sodium (23 grams) is dissolved in alcohol (300 grams), the solution of sodium ethoxide mixed with ethylic cyanacetate (113 grams), ethylic dimethylacrylate (129 grams) is then added, and the whole heated in a reflux apparatus on the water bath. The sodium derivative of ethylic cyanoacetate, which at first separates as a white, crystalline powder, slowly dissolves, and the liquid darkens and gradually sets to an almost solid cake of the sodium derivative of the condensation product, the reaction being finished in about 24 hours. Water is now added, and the oily condensation product extracted with ether in the usual way; the ethereal solution, after washing with water and drying over calcium chloride, deposits a thick oil which, after two distillations under reduced pressure, passes over constantly at 190° (30 mm.), and consists of pure ethylic cyanodimethylglutarate.

0.2614 gave 13.5 c.c. nitrogen at 20° and 750 mm. N = 5.80. $C_{12}H_{10}NO_4$ requires N = 5.81 per cent.

The yield of this substance produced in the above reaction is about 15 per cent. of the theoretical.

The principal product formed in this condensation is the acid ethylic salt of the substance just mentioned, that is, sthylic hydrogen a-cyano- $\beta\beta$ -dimethylglutarate, COOH·CH(CN)·C(CH₃)₂·CH₂·COOC₂H₅; this is obtained on acidifying the mother liquors of the condensation product mentioned above and extracting with ether. After thoroughly washing the ethereal solution, drying over calcium chloride and evaporating the ether, a thick oil is left, which was not analysed, since, for reasons stated below, it cannot be purified by distillation, and it showed no signs of crystallising. The yield of this substance formed is no less than 60—70 per cent. of the theoretical.

^{*} This immensely increased yield is not confined to this condensation, since it has been found that a similar result is obtained when other unsaturated ethereas salts, such as ethylic crotonate, ethylic methylacrylate, &c., are employed, and the products formed in this way are at present being investigated by one of us.

It is very difficult to understand why this acid ethereal salt should be produced in such large quantities; its formation is certainly not due to the presence of water, as several careful experiments which were made with specially dried alcohol gave, in every case, the same yield.

When distilled under ordinary pressures, this acid ethereal salt is readily decomposed, with elimination of carbon dioxide and formation of ethylic γ -cyano- $\beta\beta$ -dimethylbutyrate, $\text{CN}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_8)_2\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$, which is a mobile oil distilling without decomposition at 244°.

0.2783 gave 21.8 c.c. of nitrogen at 20° and 735 mm. N = 8.66. $C_9H_{15}O_2N$ requires N = 8.28 per cent.

When digested with concentrated hydrochloric acid in a reflux apparatus, it rapidly dissolved, and on cooling and mixing with an equal bulk of water, a mass of crystals separated, which, on examination, was found to consist of the imide of dimethylglutaric acid.

$$\beta\beta$$
-Dimethylglutarimide, $(CH_8)_2C < CH_2 \cdot CO > NH$.

This substance is produced by the hydrolysis either of ethylic a-cyanodimethylglutarate or hydrogen ethylic cyanodimethylglutarate, the process in the two cases being somewhat differently conducted. When the first or neutral ethylic salt is employed, the pure substance (60 grams) is heated with methyl alcoholic potash (50 grams) for 2 hours, the solution evaporated until free from alcohol, acidified, and extracted with ether. After evaporating the ether, the residue, which probably consists principally of cyanodimethylglutaric acid, is digested in a reflux apparatus with concentrated hydrochloric acid for 3 hours, when, on evaporating, the whole becomes filled with colourless needles of the imide; these are collected with the aid of the pump and recrystallised from water. In the case of the hydrogen ethylic salt, it is only necessary to boil with an equal volume of concentrated hydrochloric acid for 3 hours, in order to get directly an almost quantitative yield of the imide, care being taken to so moderate the reaction as to avoid loss from the evolution of carbonic anhydride, which is apt to become very vigorous.

ββ-Dimethylglutarimide crystallises from water in long, colourless needles, which melt at 144°, and at a higher temperature distilunchanged. It is very sparingly soluble in cold water, readily in hot water, and is almost insoluble in dry ether.

0.3034 gave 26 c.c. nitrogen at 17° and 750 mm. N = 9.82. $C_7H_{11}NO_2$ requires N = 9.93 per cent,

This imide is quantitatively converted into $\beta\beta$ -dimethylglutaric acid (m. p. 101°) on heating in a closed tube with concentrated hydrochloric acid for 5 hours at 200°, or by heating with dilute sulphuric acid (50 per cent.) for 3 hours on a sand bath, the acid being readily obtained from the products of hydrolysis by extraction with ether in the usual way.

$$ββ$$
-Dimethylghutaric Anhydride, $CH_2 \cdot C(CH_3)_2 \cdot CH_2$.

This anhydride has already been obtained from the acid by treatment with acetic anhydride (Trans., 1896, 69, 1475), but the process used in the production of the acid and conversion of this into the anhydride has subsequently been much improved, and very large quantities have been prepared for the purposes of this research by the following method. Ethylic cyanodimethylglutarate, as well as the acid ethylic salt, which is always the chief product in the condensation of ethylic cyanoacetate with ethylic dimethylacrylate, are boiled with an equal volume of 50 per cent. sulphuric acid for 12 hours on the sand bath. The exact end point of the reaction is difficult to determine, owing to the fact that the sulphuric acid converts a large proportion of the dimethylglutaric acid into anhydride, and this, like the unhydrolysed ethylic salts, floats on the surface of the aqueous liquid as on oil; we found, however, that 12 hours was sufficient to ensure complete hydrolysis.

The product, when cold, is extracted several times with ether, the ether distilled off, and the residue, without further purification, mixed in the same flask with an equal bulk of acetic anhydride, and boiled for 3 hours on a sand bath, using a reflux condenser. After distilling off most of the acetic anhydride under the ordinary pressure, the crude dimethylglutaric anhydride which remains is purified by fractionation under reduced pressure, when almost the whole passes over at 181° (25 mm.) as a colourless oil, which, on cooling, solidifies to a hard, crystalline cake.

The yield of pure anhydride obtained in this way was over 90 per cent. of theory calculated from the ethylic cyanodimethylglutarate, or about 73 per cent. calculated from the ethylic cyanoacetate originally used in the condensation.

Action of Bromine on Dimethylglutaric Anhydride.—In investigating this reaction, dimethylglutaric anhydride was treated with phosphorus pentabromide and bromine, and the bromo- or dibromo-acid bromides thus produced were converted into methylic or ethylic salts by the action of methylic or ethylic alcohols.

Ethylic a-bromo-ββ-dimethylglutarate, COOC₂H₅·CHBr·C(CH₈)₉·CH₂·COOC₂H₅, was prepared from dimethylglutaric anhydride (13 grams) by mixing it with phosphorus pentabromide (50 grams), and heating the mixture in a reflux apparatus on the water bath until the reaction was complete; bromine (16 grams) was then gradually added, and as soon as the vigorous evolution of hydrogen bromide had ceased the whole was heated on the water bath until colourless, and the product poured into well-cooled absolute alcohol. After being allowed to stand for some hours, water was added, when a heavy oil was precipitated which was extracted with ether, and the ethereal solution, after washing well with sodium carbonate solution, was dried over calcium chloride and evaporated. The nearly colourless heavy oil thus obtained, on fractionation, distilled constantly at 181° (20 mm.), and consisted of pure ethylic bromodimethylglutarate.

0.1820 gave 0.0669 AgBr. Br = 27.23. $C_{11}H_{19}BrO_4$ requires Br = 27.11 per cent.

Hydrogen Ethylic Salt of α-Bromo-ββ-dimethylglutaric Acid, COOH·CHBr·C(CH₃)₂·CH₂·COOC₂H₅.

This is precipitated in considerable quantity when hydrochloric acid is added to the sodium carbonate washings obtained as explained in the last paragraph. It is a heavy, colourless oil which distils without decomposition at 240° (35 mm.).

0.1932 gave 0.0771 AgBr. Br = 29.80. $C_0H_{15}BrO_4$ requires Br = 29.97 per cent.

The formation of this acid ethylic salt in the proportion of about 20 per cent. of the total product of bromination is not due to the presence of water in the alcohol used, as is shown by the fact that exactly the same amount was formed in an experiment in which extra precautions were taken to eliminate, as far as possible, every trace of water. It seems to us probable that, from the examination of a number of similar cases, some acid bromides have the power of decomposing alcohol in such a way as to form the free acid and ethylic bromide, thus: $R \cdot COBr + HO \cdot C_9H_5 = R \cdot COOH + C_9H_5Br$.

It is also possible that the position of the bromine atom may account for the difficulty with which this hydrogen ethylic salt is further etherified, as an experiment which we made with the object of converting the hydrogen ethylic salt into the neutral ethereal salt, by means of alcohol and hydrogen chloride, showed that very little etherification had taken place.

Methylic a-bromo-ββ-dimethylglutarate,

 $\mathbf{COOCH_3 \cdot CHBr \cdot C(CH_3)_2 \cdot CH_2 \cdot COOCH_3},$

s obtained when the bromo-acid bromide of dimethylglutaric acid,

prepared as explained above, is poured into well cooled methylic alcohol. It is a mobile liquid boiling at 172° (20 mm.).

This interesting substance, which is isomeric with the caronic acids, was prepared as follows.

The hydrogen ethylic salt of bromodimethylglutaric acid (20 grams) was dissolved in dilute sodium carbonate and boiled in a reflux apparatus on a sand bath, care being taken that the solution always had a distinctly alkaline reaction. As soon as a small quantity of the liquid gave no precipitate with hydrochloric acid, the whole was acidified, saturated with ammonium sulphate, and repeatedly extracted with ether; the dried ethereal solution, when evaporated, gave a hard, crystalline mass which, on being left in contact with porous porcelain for some days, became quite colourless and melted at 80-100°. order to purify this crude product, and especially with the object of determining whether it contained any trans-caronic acid (p. 59), the lactone was dissolved in a slight excess of ammonia, evaporated on the water bath, and the well dried ammonium salt warmed with absolute alcohol, when the whole dissolved readily, showing that no trans-caronic acid was present. Ether was then added to the alcoholic solution until a slight turbidity was produced, and the fine, transparent prisms of the pure ammonium salt deposited on standing were collected, washed, and converted into the acid, which was further purified by repeated recrystallisation first from benzene and then from water. Analysis.

0.1643 gave 0.3225 CO₂ and 0.0932 H₂O. C = 53.53; H = 6.30. $C_7H_{10}O_4$ requires C = 53.16; H = 6.33 per cent.

This lactone melts at 112°, and when heated in a small retort distils without change. It is readily soluble in ether, acetone, ethylic acetate, and hot benzene, moderately in chloroform, and almost insoluble in light petroleum.

Action of Alcoholic Potash on Ethylic a-Bromo-ββ-dimethylglutarate.

Formation of cis- and trans-Caronic Acids.

$$C(CH_8)_2$$
 COOH-CH-COOH.

In this interesting experiment, the brom-ethereal salt (15 grams) was digested in alcoholic solution with caustic potash (15 grams) for

10 hours, and the product, after being freed from alcohol by evaporation on the water bath with the addition of water, was dissolved in water, acidified, and extracted several times with ether. On distilling off the ether, a syrupy mass was obtained, which became partially solid on standing: this was dissolved in a little water and saturated with hydrogen chloride, when the crystalline solid, which slowly separated after being collected and dried on a porous plate, melted indefinitely between 170° and 200°. This crude substance was dissolved in ammonia, evaporated to dryness, and the residual solid ammonium salt ground up with cold absolute alcohol; a small quantity passed into solution, but most of it remained undissolved.* The insoluble salt was collected, washed with absolute alcohol. dissolved in a little water, acidified and extracted with ether; the ethereal solution, on evaporating, deposited a solid acid which even before recrystallising melted at 210-212°, and after recrystallising from water at 213°. This substance is trans-caronic acid. alcoholic filtrate from the insoluble ammonium salt of trans-caronic acid, on being mixed with ether and allowed to stand, deposited a small quantity of crystalline solid; this, after collecting, acidifying, and extracting with ether, yielded an acid melting at 176°, which, doubtless, consisted of cis-caronic acid (m. p. 176°), but the quantity was too small for analysis. In this hydrolysis, therefore, both the caronic acids appear to be formed, but the trans-modification in far larger quantity than the cis-modification.

On evaporating the solution after the precipitation of the cis- and trans-caronic acids to dryness with ammonia, and dissolving the residue in alcohol, an oily ammonium salt was precipitated on the addition of much ether, which, on long standing, became solid; from this, on acidifying, a considerable quantity of the lactone of hydroxy-dimethylglutaric acid was obtained, melting at 112°.

Action of Potash on the Hydrogen Ethylic Salt of a-Bromo-ββ-dimethylglutaric Acid.

This hydrolysis, which gives by far the best yield of trans-caronic acid, was conducted as follows. Equal weights of the brom-ethereal salt and caustic potash were heated together in alcoholic solution in a reflux apparatus for 3 hours, and after evaporating the alcohol, acidifying, and extracting with ether, exactly as explained in the last experiment, a hard, solid, crystalline cake was obtained; this, on being crystallised once from water, melted at 213°, and consisted of pure trans-caronic acid. On treating this acid and its mother liquors

This salt is the acid ammonium salt of trans-caronic acid, and has the formula C₇H₁₂NO₄ (Baeyer, Ber., 1896, 29, 2800).

with ammonia and alcohol, as explained above, we were not able to extract even traces of the cis-modification or of the lactone of hydroxydimethylglutaric acid.

It is remarkable that hydrogen ethylic bromodimethylglutarate should behave so differently from the normal ethylic salt on treatment with potash under the same conditions, and that in the latter case, besides trans-caronic acid and traces of the cis-modification, such considerable quantities of the lactone of hydroxydimethylglutaric acid should be produced.

The formation of trans-caronic acid from the hydrogen ethylic salt seems to us to prove that this salt has the formula

COOH·CHBr·C(CH₈)₂·CH₂·COOC₂H₅,

given to it on p. 50, and that elimination of hydrogen bromide takes place before hydrolysis. If this ethereal salt had the alternative formula, COOC₂H₅·CHBr·C(CH₃)₂·CH₂·COOH, the elimination of hydrogen bromide would be expected to take place between the bromine atom and the hydrogen atom of the carboxyl group, and the lactone of hydroxydimethylglutaric acid would be formed; this, however, is not the case.

Action of Diethylaniline on Ethylic Bromodimethylglutarate.—As it has frequently been found that diethylaniline is a very valuable reagent for removing hydrogen bromide from organic substances, it was thought that interesting results might be obtained if its behaviour were investigated in the present instance. Accordingly, 50 grams of ethylic bromodimethylglutarate was boiled in a reflux apparatus with 75 grams of pure diethylaniline for 2 hours, and after cooling, the nearly solid product was treated with dilute hydrochloric acid, and the oil which separated extracted with ether. The ethereal solution was dried, evaporated, and the residual oil fractionated a great many times, first under reduced and then under the ordinary pressure. It was thus separated into two fractions which boiled at 241° and at about 265—275°.

The oil boiling at 241°, on analysis, gave the following numbers.

0.1345 gave 0.3032 CO_2 and 0.1087 H_2O . C = 61.48; H = 8.98. $C_{11}H_{18}O_4$ requires C = 61.68; H = 8.41 per cent.

Since this oil, on hydrolysis, yielded trans-caronic acid, it is evidently the ethereal salt of this acid.

The fraction 265—275°, which was not analysed, gave, on hydrolysis, the lactone of hydroxydimethylglutaric acid, and is evidently the ethereal salt of this lactonic acid. These two substances were obtained in about equal quantities.

The synthetical acid has properties identical with those described by Baeyer and Villiger (Ber., 1896, 29, 2800) as characteristic for the acid from carone. It is sparingly soluble in cold water, but readily in hot water, and separates from its hot solution in prisms which melt at 213°. It is very sparingly soluble in ether, benzene, and cold water, and almost insoluble in chloroform and light petroleum.

0.1504 gave 0.2913
$$CO_2$$
 and 0.0888 H_2O . $C = 52.82$; $H = 6.56$. $C_7H_{10}O_4$ requires $C = 53.16$; $H = 6.33$ per cent.

The silver salt is precipitated as a white, crystalline powder when silver nitrate is added to a neutral solution of the ammonium salt.

0.2660 gave 0.2177 CO₂, 0.0547 H₂O and 0.1538 Ag. C = 22.33; H = 2.29; Ag = 57.82.

 $C_7H_8O_4Ag_2$ requires C = 22.57; H = 2.15; Ag = 58.06 per cent.

trans-Caronic acid does not give an anhydride when digested with acetic anhydride, but when heated with acetic anhydride at 220° it yields the anhydride of cis-caronic acid (p. 61). That it is a saturated acid is shown by the fact that its solution in sodium carbonate does not reduce permanganate.

It was stated in the introduction to this paper that one of the most remarkable reactions of trans- and cis-caronic acid discovered by Basyer, was the transformation of these acids into terebic acid by the action of hydrobromic acid at 100°, and it was consequently of importance to show that the synthetical acids behaved in the same manner under the same conditions.

About 0.5 gram of pure synthetical trans-caronic acid was heated with about 5 c.c. of concentrated hydrobromic acid (saturated at 0°) for 5 hours at 100°; the hydrobromic acid was then removed by evaporation on the water-bath, and the residue recrystallised from water; the colourless, cubic crystals melting at 174° thus obtained gave the following numbers on analysis.

0.1422 gave 0.2757 CO_3 and 0.0802 H_2O . C = 52.87; H = 6.26. $C_7H_{10}O_4$ requires C = 53.16; H = 6.33 per cent.

Terebic acid has the same empirical formula and the same melting point as cis-caronic acid, but in other respects these acids possess very different properties, and there can be no doubt that the acid obtained in the above experiment was terebic acid, and not unchanged ciscaronic acid, for the following reasons (compare Baeyer, Ber., 1896, 29, 2799). This acid yields an ammonium salt which differs from the ammonium salt of cis-caronic acid in that, besides having a different crystalline form, its solution in alcohol is not precipitated by ether. It gives, with silver oxide, a silver salt which is readily soluble in water and crystallises in needles, and on boiling with baryta water it yields the characteristic crystalline barium salt of diaterebic acid. Finally, a small quantity heated in a test tube gave the odour of pyroterebic acid,

$$\begin{array}{ll}
O & \longrightarrow & C(CH_3)_2 \\
CO \cdot CH_2 \cdot CH \cdot COOH
\end{array} = COOH \cdot CH_2 \cdot CH : C(CH_3)_2 + CO_2,$$

and the residue, dissolved in soda, instantly reduced permanganate, a behaviour not shown by cis-caronic acid, which, under these conditions, is simply converted into its anhydride.

Conversion of trans-Caronic Acid into cis-Caronic Acid.

This conversion, which had not previously been observed, may be readily accomplished in the following way. trans-Caronic acid is mixed with three times its weight of freshly distilled acetic anhydride, and the mixture heated in a sealed tube for 6 hours at 220°. The dark brown product is then freed from the excess of acetic anhydride by distillation, the residue dissolved in boiling water, digested with animal charcoal, filtered, and evaporated to a small bulk; on cooling, large, glistening, colourless crystals separate, which melt at 176°, and consist of pure cis-caronic acid.

0.1602 gave 0.3108 CO₂ and 0.0900 H₂O. C = 52.91; H = 6.24. $C_7H_{10}O_4$ requires C = 53.16; H = 6.33 per cent.

$$C(CH_8)_8$$
 cis-Caronic acid, HC
 CH
, is very sparingly soluble in $COOH$ $COOH$
old water, but readily in hot water, and crystallises from water

cold water, but readily in hot water, and crystallises from water most beautifully in brilliant, glistening plates with bevelled edges. It is sparingly soluble in dry ether and in light petroleum, and practically insoluble in chloroform; it dissolves readily in sodium carbonate, and this solution does not decolorise permanganate. When heated above its melting point, ois-caronic acid is rapidly converted into its

anhydride. The ammonium salt of cis-caronic acid is readily obtained by dissolving the acid in excess of aqueous ammonia and evaporating the solution on a water bath. The crystalline residue differs most sharply from the ammonium salt of the trans-acid in being readily soluble in absolute alcohol; from its alcoholic solution, it is precipitated by ether in the form of slender needles. When cis-caronic acid is heated with hydrobromic acid, under the conditions given in detail in the corresponding experiment with the trans-acid (p. 59), it is converted into terebic acid melting at 174°.

It will be seen from this short description of the properties of ciscaronic acid that the synthetical acid is identical with the acid obtained by Baeyer (loc. cit.) from carone.

formed either when cis-caronic acid is distilled, or when trans-caronic acid is heated at 220° with acetic anhydride, but it is best prepared by boiling cis-caronic acid with acetyl chloride until hydrochloric acid ceases to be evolved, evaporating, and crystallising the residue from dry ether, when lustrous plates are obtained which melt at 56°.

There can be no doubt that this is the anhydride of the cis-acid, because it is, as Baeyer found (loc. cit., p. 2799), quantitatively converted into the acid on boiling with water.

The authors wish to state that this research was carried out with the aid of a grant from the Royal Society Research Fund, and that they are indebted to Mr. F. H. Lees for making most of the analyses given in this and the succeeding communication.

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VII.—Synthesis of a\(\beta\beta\)-Trimethylglutaric Acid. COOH·CH(CH₂)·C(CH₂)₂·CH₂·COOH.

By W. H. PERKIN, jun., and Jocelyn F. Thorpe.

Or the four theoretically possible trimethylglutaric acids, two only, up to the present, have been prepared synthetically, namely, the ααα₁-acid, COOH·C(CH₈)₂·CH₂·CH(CH₈)·COOH, by Auwers and Victor Meyer (Bor., 1890, 23, 293) from ethylic α-bromisobutyrate and "molecular" silver, and the ααβ-acid, COOH·C(CH₈)₂·CH(CH₈)·CH₂·COOH,

which was prepared by us (Trans., 1897, 71, 1187), by the reduction of the corresponding trimethylglutaconic acid,

The remaining two acids are

$$a\beta\beta$$
 COOH·CH(CH₃)·C(CH₂)·CH₂·COOH, and $a\beta a_1$ COOH·CH(CH₃)·CH(CH₂)·CH(CH₃)·COOH.

Of these, the first has a special interest, for the following reason.

By the oxidation of camphoric acid with permanganate at the ordinary temperature, Balbiano (*Ber.*, 1894, 27, 2133; 1897, 30, 1908), obtained an acid of the formula $C_8H_{12}O_5$, to which he assigned the constitution

This acid, on reduction, yielded a lactonic acid of the probable formula

$$\begin{array}{ccccc} \mathrm{CH}(\mathrm{CH_3}) \cdot \mathrm{C}(\mathrm{CH_3})_2 \cdot \mathrm{CH} \cdot \mathrm{COOH}, \\ \mathrm{CO} & & & & \end{array}$$

and this, by further reduction with hydriodic acid, was converted into an acid, $C_8H_{14}O_4$, which Balbiano considered to be $a\beta\beta$ -trimethylglutaric acid, because, on oxidation, it yielded aa-dimethylsuccinic acid.

Assuming that this acid is $a\beta\beta$ -trimethylglutaric acid, its formation from camphoric acid is important, as affording evidence that the latter contains the group $\text{C}\cdot\text{C}(\text{CH}_8).\text{C}(\text{CH}_8)_2\cdot\text{C}\cdot\text{C}$, a conclusion which, together with results obtained from the great amount of work which has been done on camphoronic acid, throws much light on the constitution of camphoric acid (compare Trans., 1898, 73, 797).

It thus became an important matter to be certain that the formula Balbiano assigned to his acid is correct, and for this reason we have, ever since the publication of his paper, been endeavouring to synthesise $a\beta\beta$ -trimethylglutaric acid, and it is only quite lately that we have been able to accomplish this.

In the first place, we found, as the result of a great many experiments, that it seems to be impossible to introduce a methyl group into ethylic dimethylpropanetricarboxylate,

at the point marked \bullet , by the action of sodium ethoxide and methylic iodide. Arguing from analogy to other mono-substitution products of ethylic malonate, this experiment should have yielded an ethereal salt which would have given $\alpha\beta\beta$ -trimethylglutaric acid on hydrolysis

and elimination of carbon dioxide, but, although tried under very varied conditions, no trace of this acid was obtained.

It was then thought possible that the ethylic trimethylpropanetricarboxylate, $(COOC_2H_5)_2C(CH_3)_2\cdot C(CH_3)_2\cdot CH_2\cdot COOC_2H_5$, which should have resulted from the above experiment, might be formed by the condensation of ethylic dimethylacrylate with the sodium derivative of ethylic methylmalonate, but the experiments made in this direction did not yield a trace of the desired compound, and many other syntheses, which need not be mentioned here, also gave negative results. Ultimately, we discovered the following synthesis, which is so easily carried out that large quantities of $\alpha\beta\beta$ -trimethylglutaric acid can now be obtained in a short space of time.

The method consists in heating together ethylic dimethylacrylate and the sodium derivative of ethylic cyanacetate in alcoholic solution until the condensation to the sodium derivative of ethylic cyanodimethylglutarate, which probably has the formula,

$$COOC_2H_5 \cdot C(CN)Na \cdot C(CH_8)_2 \cdot CH_2 \cdot COOC_2H_5$$
, is complete (see p. 52).

The crude product is then directly treated with methylic iodide, when an almost quantitative yield of ethylic cyanotrimethylglutarate, $COOC_2H_5$ · $C(CH_3)(CN)$ · $C(CH_3)_2$ · CH_2 · $COOC_2H_5$, is obtained. This, on hydrolysis with methyl alcoholic potash or hydrochloric acid, yields the beautiful, crystalline *imide* of $\alpha\beta\beta$ -trimethylglutaric acid,

$$C(CH_3)_2 < CH(CH_3) \cdot CO > NH$$

which, when heated with hydrochloric acid, at 200° , is converted quantitatively into $\alpha\beta\beta$ -trimethylglutaric acid.

A direct comparison of the acid thus synthesised with that obtained from camphoric acid was rendered possible by the kindness of Professor Balbiano, who sent us a sample of the acid which he was the first to prepare.

Both acids melted at 87°, and on treatment with acetyl chloride yielded the same anhydride melting at 82°, and from this by the action of aniline an anilic acid was prepared which in both cases melted at 150—151°, so that there can be no doubt as to the identity of the synthetical acid and Balbiano's acid.

In experimenting with $\alpha\beta\beta$ -trimethylglutaric anhydride, it was found that, not only does it crystallise from water unchanged, but that it actually crystallises with water of crystallisation, in prisms melting at 61°, and without being converted into the acid.

This is certainly a very unusual property of an anhydride, and the only somewhat similar case which we have been able to find is that of the β -lactone of dimethylmalic acid, $(CH_3)_2C--CH\cdot COOH$, which,

as Baeyer and Villiger (Ber., 1897, 30, 1955) have shown, crystallises with 1H₂O.

We are at present engaged in investigating other condensations between unsaturated ethereal salts and α -cyano-ethereal salts, and also on the action of halogen compounds on the sodium derivative of ethylic cyanodimethylglutarate, and we are especially interested in the ethereal salt which this sodium derivative yields on treatment with ethylic bromacetate, because, if Baeyer's formula for isocamphoronic acid be correct, this should lead to a synthesis of this very important acid.

Ethylic a-Cyano-
$$a_1$$
- $\beta\beta$ -trimethylglutarate,
COOC₂H₅·CH(CN)·C(CH₈)₂·CH(CH₈)·COOC₂H₅.

In order to prepare this substance, ethylic dimethylacrylate is digested in alcoholic solution with the sodium derivative of ethylic cyanacetate, as explained on page 52, and after heating for 15 hours excess of methylic iodide is added and the boiling continued until the liquid has a neutral reaction; water is then added, and the oily product extracted with ether. The ethereal solution, after washing well with water, drying over calcium chloride, and evaporating, deposits a thick oil which, after twice fractionating, boils constantly at 181° (25 mm.), and consists of pure ethylic cyanotrimethylglutarate.

0.22 gave 11.8 c.c. nitrogen at 23° and 750 mm.
$$N = 5.94$$
. $C_{18}H_{21}NO_4$ requires $N = 5.50$ per cent.

The yield of this pure ethereal salt obtained in this condensation is about 68 per cent. of the theoretical, and it is remarkable that, in this case, only traces of an acid ethereal salt are formed, whereas, as explained on p. 52, if the condensation is worked up before the treatment with methylic iodide the principal product is the acid ethereal salt.

$$a\beta\beta\text{-}\textit{Trimethylglutarimide}, C(CH_3)_2 < \begin{matrix} CH(CH_8) \cdot CO \\ CH_2 \end{matrix} \\ \hline CO \end{matrix} > NH.$$

This substance is formed when ethylic cyanotrimethylglutarate is hydrolysed either with methyl alcoholic potash or with concentrated hydrochloric acid; in the former case, the product often consists of the acid amide, a white, deliquescent solid which, however, can readily be converted into the imide by boiling for a short time with concentrated hydrochloric acid. $a\beta\beta$ -Trimethylglutarimide is sparingly soluble in cold, but readily in hot water, and crystallises in long needles closely resembling $\beta\beta$ -dimethylglutarimide (p. 53) in appearance. It melts at 126°.

0.1163 gave 9.4 c.c. nitrogen at 22° and 765 mm. N = 9.20. $C_8H_{13}NO_2$ requires N = 9.03 per cent.

Silver salt, C(CH₃)₂ CH(CH₃)·CO NAg.—This interesting salt is obtained as a beautiful, crystalline precipitate when dilute ammonia is carefully added to a warm solution of the imide and silver nitrate.

0.0874 gave 0.0363 Ag. Ag = 41.53. $C_8H_{12}O_2NAg$ requires Ag = 41.22 per cent.

 $a\beta\beta$ -Trimethylglutaric acid, COOH·CH(CH₈)·C(CH₈)₂·CH₂·COOH.

This acid is best prepared from the imide just described by heating it with three times its weight of concentrated hydrochloric acid in a sealed tube for 5 hours at 200°. The product is evaporated to dryness on the water bath, and the residue extracted with ether; after drying over calcium chloride, the ethereal solution deposits the acid in an almost pure condition on evaporation. For the analysis, the acid was crystallised from water, from which it separates in glistening plates melting at 88°.

0.1316 gave 0.2675 CO_2 and 0.0960 H_2O . C = 55.43; H = 8.23. $C_8H_{14}O_4$ requires C = 55.17; H = 8.05 per cent.

aeta eta-Trimethylglutaric Anhydride, $CH(CH_3) \cdot C(CH_8)_2 \cdot CH_2$.—This,

which is the most characteristic derivative of $\alpha\beta\beta$ -trimethylglutaric acid, is readily prepared by digesting the pure acid for a short time with excess of acetyl chloride, and then evaporating to dryness on the water bath. The crystalline residue, which consists of the almost pure anhydride, crystallises from a mixture of ethylic acetate and light petroleum in prisms which melt at 82°.

0.1445 gave 0.3248 CO₂ and 0.0991 H₂O. C = 61.34; H = 7.62. $C_8H_{12}O_8$ requires C = 61.54; H = 7.67 per cent.

This anhydride is quite insoluble in cold dilute sodium carbonate solution, and is only very slowly converted into the acid even on boiling.

If this anhydride is boiled with a large quantity of water, and the clear solution, rapidly poured off from the oily drops, is allowed to cool, a small quantity of the anhydride crystallises out in needles (I); the same substance is produced on melting the anhydride under hot water and stirring vigorously until it becomes solid (II). The product in both cases melts at 61°, and consists of the anhydride with half a molecule of water of crystallisation. The following are the results of the analyses of specimens of I and II.

- I. 0.2322 gram, after drying on a porous plate for 3 hours, lost 0.0134 gram at 50° . $H_{\circ}O = 5.8$ per cent.
- II. 0.4712, heated at 50° until constant, lost 0.0242. $H_2O = 5.15$. $C_8H_{12}O_8 + \frac{1}{2}H_2O$ requires $H_2O = 5.4$ per cent.

The water of crystallisation is given off rapidly on gently warming, and slowly over sulphuric acid in a vacuum desiceator; the residue then melts at 82°, the melting point of the dry anhydride.

aββ-Trimethylglutaranilic Acid,

 $C_6H_5 \cdot NH \cdot CO \cdot CH(CH_8) \cdot C(CH_8)_2 \cdot CH_2 \cdot COOH(?).$

On the addition of aniline to a solution of the anhydride in benzene, this compound separates after some time as a white, crystalline precipitate. After being purified by recrystallisation from dilute methylic alcohol, from which it separates in long needles, it melted at 150—151°, and, on analysis, gave the following result.

0.2515 gave 12.2 c.c. nitrogen at 21° and 752 mm. N=5.47. $C_{14}H_{19}NO_8$ requires N=5.60 per cent.

Our thanks are due to Messrs. F. Howles and F. H. Lees, for much valuable help in connection with this and the preceding research, and we wish also to state that the very considerable expense which these experiments have entailed has been largely met by grants from the Royal Society Research Fund.

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VIII.—Occurrence of Orthohydroxyacetophenone in the Volatile Oil of Chione glabra.

By WYNDHAM R. DUNSTAN, F.R.S., and T. A. HENRY, Salters' Research Fellow in the Laboratories of the Imperial Institute.

Some years ago, one of us (Dunstan, Proc. Roy. Soc., 46, 211) showed that the strong feecal odour of the wood of Celtis reticulosa is due to the presence of skatole, the substance to which the odour of human excrement is due. Through the interest of Mr. Thiselton Dyer, the Director of Kew Gardens, other plants having strong odours were then examined, but no definite information as to their constituents could be obtained, owing to the small quantity of material available for examination. Amongst these plants was a small specimen of the wood of Chione glabra, which had been sent to Kew by Mr. J. H. Hart, F.L.S., Superintendent of the Royal Botanic Gardens, Trinidad, with the suggestion that an examination of its constituents should be

undertaken, as the plant is reputed to possess valuable properties as a medicine and, in particular, is stated to be a powerful aphrodisiac. The bark and wood emitted a strong, unpleasant odour, chiefly aromatic, but partly feecal. This was proved to be due to an oil which was volatile with steam, and although its chief physical and chemical properties were ascertained, the constitution of its principal constituent could not be determined owing to insufficiency of material. A further supply of the wood was afterwards obtained from the collections of the Imperial Institute. This was part of a large log which had been sent previously for exhibition at the World's Fair at Chicago. Now, however, it has completely lost its characteristic odour, owing to the escape of the volatile oil, and it proved to be quite useless for our purpose. Through the kind offices of Mr. Hart, the Trinidad Government undertook the collection of a fresh quantity of the wood, which has made it possible for us to complete the inquiry by identifying the odorous constituent of the tree, and in fact, proving its identity with the substance prepared synthetically in the laboratory.

The genus Chione of the Natural Order Rubiaceae includes plants which are confined almost exclusively to the West Indies. The species Chione glabra, which is indigenous to Grenada, is a large flowering tree, known in the island as "Violette," a name which probably has reference to the aromatic smell of the flower. Through the kindness of Mr. E. J. Millard, F.C.S., we have received from Grenada a dried specimen of the stem, leaves, and flowers of this tree. The somewhat aromatic, somewhat fœcal, smell is associated with the bark and wood, especially with the former; on exposure to air, it gradually disappears. The results of the chemical investigation described in the subsequent part of this paper show that the volatile oil, which exhibits in a concentrated form the remarkable odour of the wood, is composed of two substances, the one a yellow oil boiling at 160° under 34 mm. pressure, and solidifying at low temperatures to a crystalline mass; the other, a colourless, crystalline substance melting at 82°. The former, which is the chief constituent, we have proved to be orthohydroxyacetophenone, OH. C. H. CO. CH, and is identical with the compound prepared synthetically. The crystalline substance, which is present in very small quantity, has all the properties of an alkyl derivative of the oil; the amount of substance obtained, however, was insufficient to enable us to complete the examination. The feecal odour of the fresh wood, which seems rather more pronounced than that of the constituents we have isolated from the oil. suggested the possibility that the plant might also contain a minute quantity of skatole or some other derivative of indole; but although the volatile oil contains traces of some nitrogenous substance, we have not been able to isolate any indole derivative from it. It is, however,

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interesting, and possibly significant from the biological standpoint, to observe that derivatives of orthohydroxyacetophenone may, by processes involving condensation and elimination of water, pass into compounds belonging to the indole group; the production of indoxyl from orthacetylamidoacetophenone has, indeed, been accomplished by von Baeyer and Bloem (Ber., 1884, 17, 963), and it is not difficult to conceive that the conversion may occur without difficulty and by shorter steps in the plant. The precursors of skatole and other indole derivatives in plants are at present unknown, but the occurrence of derivatives of acetophenone in the vegetable kingdom and particularly in Chione glabra, whose wood emits a feecal odour, indicates at least one possible direction in which search might be made.

Besides those whose names we have already mentioned, we are greatly indebted to Miss L. E. Boole, F.I.C., who conducted much of the preliminary examination of the constituents of this plant.

Extraction of the Volatile Oil.

The volatile oil was separated from the wood and bark by cutting these into fine shavings and distilling with steam; the distillate obtained was then shaken with ether, and the ethereal solution dried over calcium chloride and distilled. After removal of the ether, there remained a dark-coloured oil which distilled with some decomposition under the ordinary pressure; it was, therefore, distilled under reduced pressure, when a fraction boiling from 160° to 165°, under a pressure of 34 mm., was obtained. With the small quantity of material available, it was not possible to obtain a fraction of more definite boiling point.

Combustions of the liquid gave the following results.

The relative density of the oil is $d = 0.850 \, 15^{\circ}/4^{\circ}$.

It is slightly soluble in water, and has a peculiar and somewhat unpleasant odour, chiefly aromatic, but partly fœcal. An aqueous solution of ferric chloride produces a deep purple coloration, and bromine water a faintly yellow, crystalline precipitate. The oil dissolves in alkaline solutions, and such solutions, on evaporation, leave a crystalline salt or metallic derivative; the potassium and sodium salts crystallise in yellow plates which quickly decompose on exposure to air; acids regenerate the oil from them.

Action of various Reagents on the Oil.

Action of Acetic Anhydride.—The liquid was mixed with acetic anhydride and warmed. The viscous oil precipitated on the addition of water to the product was removed by shaking with ether, the ethereal solution dried, and the ether removed by distillation. The crystalline residue of acetyl derivative obtained on standing was then recrystallised from methylic alcohol until the melting point was constant at 88°. A combustion gave the following result.

0.1331 gave 0.3254
$$CO_2$$
 and 0.0776 H_2O . $C = 66.66$; $H = 6.4$. $C_8H_7O \cdot C_2H_8O_2$ requires $C = 67.4$; $H = 5.61$ per cent.

The substance is, therefore, a monacetyl derivative of the original liquid, and the existence of one hydroxyl group is thus proved.

Action of Hydroxylamine and Phenylhydrazine.—When an aqueous solution of hydroxylamine is added to the oil suspended in water and the mixture gently warmed, a red, resinous substance separates; this dissolves in boiling water, and the solution deposits colourless needles as it cools. These, after recrystallisation, melt at 112°, and have all the properties of an oxime of the original substance.

0.1841 gave 0.4242
$$CO_2$$
 and 0.1016 H_2O . $C = 62.8$; $H = 6.12$. $OH \cdot C_8H_7 \cdot NOH$ requires $C = 63.4$; $H = 5.96$ per cent.

A phenylhydrazone was also obtained by the action of a 10 per cent. solution of phenylhydrazine on the liquid suspended in water; after 24 hours, this mixture deposited a greenish-yellow oil which soon became crystalline. On recrystallisation, the hydrazone melted at 108°.

The production of an oxime and hydrazone indicate the presence of one ketonic group in the original substance.

Action of Bromine.—When bromine water is added to the oil suspended in water, a colourless precipitate forms immediately, and on standing becomes crystalline; after recrystallisation from hot alcohol, it melts somewhat indefinitely at 108°, or, after prolonged heating at a lower temperature, at 95°. We are lunable, at present, to represent its composition by any formula derivable from that of the parent substance. Combustions and two determinations of bromine by Carius' method gave the following results.

C.	32.6 per cent.	$\mathbf{H.}$ 2.52 per cent.	Br. 45.64 per cent.	
	32.3 "	2.04 ,,	46.2 ,,	
	32.96 ,,	2.09 ,,		
	32.89 "	2·26 "		

It will be seen that these values for carbon, hydrogen, and bromine do not agree with those required for a mono- or dibromo-derivative.

$$C_8H_7O_2Br$$
 requires $C = 44.6$; $H = 3.2$; $Br = 37.2$. $C_8H_8O_9Br_9$, $C = 32.6$; $H = 2.04$; $Br = 54.4$.

When the bromine derivative is reduced with tin and hydrochloric acid, it yields a small quantity of a phenolic substance giving a bromine derivative melting at 86°. It is possible that the solid bromo-derivative is a mixture of one or more simple bromine derivatives, but this is not very probable, since its composition seems to be constant when prepared under various conditions, and its melting point is very definite.

Action of Fused Potash.—When the oil is boiled for some time (in a vessel fitted with an upright condenser) with 10 per cent. potash solution, it merely passes into a metallic derivative, and can be recovered by acidifying the solution; and even when heated with alkaline solutions in sealed tubes at 125°, it is not decomposed. When fused with excess of potash, the potassium salt of the oil floats for a time on the excess of potash, but is subsequently completely decomposed, forming a dark brown mass. When this is dissolved in water, acidified, and the mixture distilled, a solution containing phenol is obtained; this was identified by means of its tribromo-derivative. When the acid liquid left after distillation was extracted with ether, it furnished a crystalline substance which, after recrystallisation from hot water, melted at 151°, and gave all the reactions of salicylic acid m. p. 155°).

Action of Nitric Acid.—The residue from the Carius' estimations of bromine in the bromo-derivative was examined, and found to contain oxalic acid and a yellow, crystalline substance; the quantity of the latter, however, was too small to admit of satisfactory identification, but since it dyed silk yellow and did not dye cotton, and gave the chloropicrin reaction, there can be little doubt that it was picric acid.

These observations as to the chemical behaviour of the volatile oil of *Chione glabra* prove that its chief constituent is orthohydroxy-acetophenone $[OH:CO\cdot CH_8=1:2]$.

The facts may be conveniently summarised here.

- 1. The parent substance has a composition represented by the formula $C_8H_8O_2$.
- 2. One of the hydrogen atoms can be replaced by the acetyl group, indicating the presence in the parent substance of one hydroxyl group.
- 3. The oil forms a monoxime, having a composition represented by the formula $C_8H_9O_2N$.
- 4. Fusion of the oil with potash furnished salicylic acid and phenol, the latter as the result of secondary action.

The formation of all these substances is readily explained on the assumption that the chief constituent of the oil is orthohydroxyacetophenone, OH·C₆H₄·CO·CH₈. This compound has been described by Tahara (Ber., 1892, 25, 1306) and by Feuerstein and Kostanecki (Ber., 1898, 31, 710—719). The latter chemists described orthohydroxyacetophenone (obtained by the action of alcoholic soda on phenacylidenflavene) as a yellow oil of peculiar odour, distilling at 218°, giving a purple red colour with ferric chloride solution, and forming a yellow, crystalline, sodium salt. Tahara prepared the compound by the decomposition of orthomethoxybenzoylacetic acid. The acetyl derivative melted at 89°, and the phenylhydrazone at 107°.

We have prepared oxthohydroxyacetophenone from nitrocinnamic acid, by the following series of reactions. Orthonitrocinnamic acid, NO₂·C₆H₄·CH:CH·COOH, was converted successively into dibromonitrophenylpropionic acid, NO₂·C₆H₄·CHBr·CHBr·COOH; orthonitropropiolic acid, NO₂·C₆H₄·CiC·COOH; orthonitrophenylacetylene, NO₂·C₆H₄·CiCH; orthamidophenylacetylene; NH₂·C₆H₄·CiCH; orthomidoacetophenone, NH₂·C₆H₄·CO·CH₃; and, finally, by diazotising into orthohydroxyacetophenone, OH·C₆H₄·CO·CH₃.

These compounds, with the exception of the last, have been prepared by Baeyer and Bloem (Ber., 1880, 13, 2259), and we have made use of the methods of preparation and purification described by these chemists. The orthohydroxyacetophenone thus prepared had all the characteristics of the oil distilled from Chione glabra, and furnished derivatives having the same physical constants; thus the bromine derivative and the oxime melted at 108° and 112° respectively.

Orthomethoxyacetophenons.—The quantity of colourless, crystalline substance left as a residue in the distillation of the crude chione oil was too small to admit of an extended examination, but since it was decomposed by boiling with hydriodic acid, giving a volatile iodide, with the production of an oil having the properties of orthohydroxyacetophenone, it is probably an ether, possibly the methyl ether of this substance. The minute amount of this constituent present in the volatile oil has made it impossible for us more certainly to identify it.*

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"This volatile oil is of a pale yellow colour, and has a specific gravity higher than

^{*} Since the work described in the present paper was completed, the following account of the volatile oil of *Chiome glabra* has appeared (Paul and Cownley, *Pharm. Journ.*, [iv], 7, 51). The material examined was obtained from the Windward Islands. "From the aromatic odour of the bark, it was conjectured that it might contain a volatile oil, and on examination with that object we succeeded in isolating a volatile oil amounting to about 1.5 per cent. by weight.

IX.—Occurrence of Hyoscyamine in the Hyoscyamus muticus of India.

By WYNDHAM R. DUNSTAN, F.R.S., and HAROLD BROWN, Assistant Chemist in the Laboratories of the Imperial Institute.

Hyoscyamus muticus is a species of henbane which occurs in certain districts of India, and has long been used in Indian medical practice, as a particularly virulent drug. The nature of its alkaloid, however, has never been determined.

The following account of the plant is abbreviated from that given in Hooker's Flora Indica.

H. muticus is found in the West Punjab, in Scinde, and in Cabul, westward to Egypt.

Cauline leaves, petioled, ovate or oblong, entire or toothed, lower flowers pedicelled, calyx striate, pubescent, teeth short, triangular, not acute in fruit, corolla 1 to $1\frac{1}{2}$ inches, lurid yellow or nearly white. Stem, 1 to 3 feet. Leaves, 4 to 7 inches, pubescent, or somewhat woolly, petiole $\frac{1}{4}$ to 3 inches. Lower pedicles in fruit, $\frac{1}{4}$ to 1 inch. Calyx, $\frac{2}{3}$ inch, in fruit, 1 by $\frac{1}{2}$ inch, funnel-shaped, ribbed, somewhat reticulate, villous, or ultimately glabrous; teeth short, triangular, not spreading. Capsule, $\frac{1}{4}$ inch in diameter. Seed, $\frac{1}{24}$ inch in diameter.

The medicinal effects of this drug appear to resemble those of ordinary henbane; when administered in comparatively large doses, it acts as a powerful excitant, leading to what have been described as paroxysms of mania, whence the synonym Hyoscyamus insanus. There is some reason to believe that it has been employed in the preparation of certain extremely potent kinds of the Persian "Benj" and in some varieties of the Indian "Bhang," which, however, is usually prepared from Indian hemp. Since there is at present a considerable demand for atropaceous drugs and their alkaloids, it seemed desirable to examine

that of water. It gave a mass of accoular crystals on being cooled to about -20° . The oil gave no crystalline compound with sodic bisulphite, nor could evidence be obtained of methyl salicylate. It gave a semi-solid mass on treatment with a concentrated solution of caustic soda. It is readily soluble in dilute caustic soda, and reprecipitated by acids apparently unaltered. It is slightly soluble in water, its aqueous solution gives a purple-blue coloration with ferric chloride. The volatile oil is evidently a phenol.

"There are several volatile oils having somewhat similar properties to those above described, but the quantity of oil obtained was too small to admit of the further examination which its peculiarity appears to deserve."

the alkaloid of this plant, which is fairly abundant in the districts of India in which it is found, and might possibly prove to be worth exporting.

Extraction and Estimation of the Alkaloid.

The sample, which weighed nearly two pounds, was collected in Scinde, at the instance of the Reporter on Economic Products to the Government of India, and consisted of both stems and leaves of the plant; these were separated as far as possible, but there remained a mixture of fine stems and broken leaf.

Total weight, 900 grams...
$$\begin{cases} 300 \text{ grams leaf.} \\ 310 & \text{,, stem.} \\ 290 & \text{,, mixture of leaf and stem.} \end{cases}$$

These three portions were extracted separately, in order to determine the proportion of alkaloid in each.

The material was air-dried at a low temperature, finely powdered, and then exhausted by percolation with cold alcohol, the percolate being evaporated under reduced pressure until nearly the whole of the alcohol had been removed. The semi-solid residue was then extracted with dilute hydrochloric acid (0.5 per cent.), gently warmed, and well shaken; after subsidence, the acid liquid was poured off and the treatment repeated until the alkaloid was completely removed. The acid solution, after filtration, was shaken with small quantities of chloroform in order to remove the chlorophyll, then made slightly alkaline by the addition of dilute ammonia, and the alkaloid extracted by successive shakings of the alkaline liquid with chloroform; on distilling off the chloroform under reduced pressure, a gummy, alkaloidal residue was obtained having a slight odour recalling that of pyridine.

A small quantity of alkaloid remained in the alkaline liquid, and could not be removed by agitation with chloroform; it was, however, subsequently isolated and examined.

By percolation with cold alcohol, the following percentages of alkaloid were found.

In the plant (stem and leaf), 680 grams yielded 0.7 gram of alkaloid, or 0.1 per cent. (nearly pure).

In the stem only, 310 grams yielded 0.46 gram of alkaloid (nearly pure), which is 0.15 per cent.

In the broken leaf and fine stems, 250 grams yielded 0.14 gram of alkaloid (nearly pure), which equals 0.056 per cent.

Examination of the Alkaloid.

In order to identify the alkaloid or alkaloids present, the impure amorphous residues were converted into the aurichloride, which was

examined by fractional crystallisation, as described in a previous paper on the alkaloids of Scopola Carniolica (Dunstan and Chaston, Ph. J., [iii], 20, 461); this was obtained as a yellow, pulverulent precipitate, which was recrystallised from hot water acidified with hydrochloric acid. The alkaloid from the mixed stem and leaf yielded two large fractions of auric chloride melting at 154—156° and, after recrystallising, at 157—158°, which is very near the melting point of hyoscyamine aurichloride. From the mother liquors, containing the excess of auric chloride, two very small fractions of crystals were obtained melting at 149—150° and 140—145° respectively; these were too small to be dealt with separately.

The alkaloid from the stem yielded three main fractions of aurichloride all melting between 154° and 156°. On recrystallising once, three fractions melting at 158°, 157.5° and 154-156° were obtained; by concentrating the mother liquors from these, two small fractions melting at 150-155° and 145-150° were obtained, and, finally, a few crystals melting at 141-145°. The fractions of similar melting points were combined and recrystallised from dilute acid until a constant melting point was attained. In the case of the fractions of higher melting point, two or three recrystallisations sufficed, whereas the lower fractions required the operation to be repeated at least six times before a constant melting point was obtained; by this means, practically the whole of the aurichloride originally taken was obtained in shining leaflets melting at 1595°. There only remained two small fractions melting at 157-158° and the two lowest fractions, at 140-145°, which were too small to be separately dealt with, and were consequently retained and afterwards combined with a fraction of similar melting point.

It is, therefore, proved that nearly the whole of the aurichloride is that of hyoscyamine, which melts at 160° (Ladenburg).

The small quantity of alkaloid which remained in the alkaline liquid and was not removed by agitation with chloroform was isolated in the following manner (Dunstan and Ransom, Ph. J., [iii], 14, 623). The chloroform and alcohol present were removed by distillation under reduced pressure, the liquid was acidified, and the whole of the alkaloid precipitated by adding a solution of iodine in potassium iodide; the alkaloidal periodide was collected, washed, and then decomposed by a small quantity of a solution of sodium thiosulphate, the liquid made alkaline with dilute ammonia, and the alkaloid extracted with chloroform. The small quantity of alkaloid thus obtained was converted into the aurichloride, but this could not be recrystallised and was mixed with the lowest melting fractions (above referred to) for further treatment.

Analysis of the Aurichloride.

The pure aurichloride melting at 159.5°, was analysed, the gold, chlorine, and alkaloid, being directly determined. A weighed quantity of the salt was dissolved in water, the gold precipitated as sulphide, ignited, and weighed as metal. After the hydrogen sulphide had been removed from the filtrate by passing a current of air, it was exactly neutralised with soda, and the chlorine determined by titration with centinormal silver nitrate. The filtrate from the silver chloride was concentrated in a vacuum over sulphuric acid, then made alkaline with dilute ammonia, and the alkaloid removed by agitation with chloroform, and the residue obtained on distilling off the chloroform was dried in a vacuum over sulphuric acid until its weight was constant.

I. 0.0636 aurichloride gave 0.0201 Au, and required 42.2 c.c. N/100 AgNO₈ (1.c.c. = 0.0003416 Cl). Au = 31.60; Cl = 22.66.

II. 0.0424 aurichloride gave 0.0134 Au, and required 27.8 c.c. $N/100 \text{ AgNO}_3$. Au = 31.60; Cl = 22.40.

The two solutions containing the alkaloid from both the above determinations were mixed, and the total amount of alkaloid estimated.

0.106 aurichloride gave 0.0491 alkaloid = 46.32 per cent.

	Gold.	Chlorine.	Alkaloid.
Found	31.60, 31.60	22.66, 22.40	46.32
Calculated for $C_{17}H_{23}NO_8$, $HAuCl$	4 31·34	22.54	45.95

Another specimen of aurichloride yielded, on ignition, 31.25 per cent. of gold.

From more of the pure aurichloride, the alkaloid was regenerated by the method above described, and after recrystallisation from a mixture of dry chloroform and petroleum, it was obtained in long, silky needles. These were dissolved in absolute alcohol, and the specific rotatory power determined. The solution was laworotatory.

$$a = 31'$$
. $l = 1 dm$. $c = 2.04$. $t = 19^\circ$.
whence $[a]_D = \frac{100 \times 31}{2.04 \times 60} = -25.32^\circ$.

Other observers have recorded numbers lying between 20° and 21°.

Hyoscyamus muticus as a Commercial Source of Pure Hyoscyamine.

Having thus ascertained that the alkaloid in Hyoscyamus muticus is chiefly, if not entirely, hyoscyamine, experiments were made to extract the crystalline alkaloid direct from the plant. For this purpose,

about $1\frac{1}{2}$ lbs. of the plant, both stem and leaf, was finely powdered and the alkaloid extracted by the method already described; in this way, 0.7 gram of impure alkaloid was obtained as a coloured, gummy residue, which could not be crystallised either from ether or from dilute alcohol. By dissolving in dry chloroform, however, and gradually adding light petroleum, the colouring matter was precipitated, together with a little of the alkaloid, and a nearly colourless solution was obtained, from which, on adding more petroleum and allowing it to stand, groups of small needles were gradually deposited. Several fractions of the crystalline base were thus obtained, and were recrystallised in the same manner. Finally, pure hyoscyamine was obtained in colourless, silky needles melting at 105° .

Absence of other Mydriatic Alkaloids.—The small quantity of alkaloid precipitated along with the colouring matter by the first additions of petroleum to the solution in chloroform was also examined. The precipitate was extracted with very dilute hydrochloric acid, the solution filtered, and aurichloride added, when a yellow precipitate was produced which quickly aggregated to a resinous mass (fraction A); this was removed, and on adding more of the reagent to the filtrate a yellow, pulverulent precipitate was obtained, which did not aggregate on standing (fraction B). These two fractions were recrystallised separately from dilute acid; from fraction A, two crops of crystals were obtained melting at 154—155° and 156—158° respectively; and from fraction B, crystals were obtained melting at 157—158°. The mother liquors from all these were concentrated in a vacuum, and thus a few crystals melting at 146—149° were separated.

All fractions of aurichloride insufficient for separate recrystallisation which had been obtained in the various experiments made were finally combined into two groups according to their melting points, 155—158° and 140—145° respectively. These were recrystallised as before and virtually the whole of the gold salt was found to melt constantly at 159.5°. A very small fraction melted at 158—159°, and another from 150—155°, but these were too minute for further recrystallisation. The following are the melting points of the aurichlorides of the chief mydriatic alkaloids: atropine, 136—138°, hyoscyamine, 159—160°; scopolamine or hyoscine, 198—199°.

There is, therefore, no evidence of the existence in this sample of *Hyoscyamus muticus* of any mydriatic alkaloid than hyoscyamine. We believe that the plant will prove to be an important source of this alkaloid, since it can be isolated from it with far less difficulty than from ordinary henbane (*Hyoscyamus niger*), which also contains the alkaloid hyoscine, and often atropine in addition.

It should, however, be remembered that the nature of the alkaloids contained in atropaceous plants appears to vary with age, mode of culti-

vation, and other circumstances. Thus, in belladonna, the proportion of hyoscyamine to atropine fluctuates widely with the age of the plant. It is, therefore, desirable that other specimens of *Hyoscyamus muticus* should be examined, in order to ascertain whether hyoscyamine is invariably the only alkaloidal constituent.

It will be convenient to summarise here our present information as to the occurrence of hyoscyamine in various plants.

Hyoscyamus niger and albus (hyoscyamine and scopolamine).

Hyoscyamus muticus (hyoscyamine).

Atropa belladonna (atropine, hyoscyamine, and a little scopolamine).

Datura stramonium ,, ,,

Duboisia myoporoides (hyoscyamine and a little scopolamine).

Scopola carniolica (hyoscyamine).

Scopola japonica (atropine, hyoscyamine, and scopolamine).

Lactuca sativa and virosa (hyoscyamine).

The following percentages of total alkaloid have been recorded.

	Atropa belladonna.	Datura stramonium.	Hyoscyamus niger.		Нуо зсуат ив
			Biennial.	Annual.	muticus.
	-	CO.30 0.00	0.155-0.173 {1st yr. 0.089-0.089 2nd ,, 0.045-0.068 0.058-0.1	leaves and tops 0.064—0.070 —	stem and leaf 0.1 0.46

We are indebted to Mr. E. A. Andrews, Junior Assistant in these Laboratories, for the skilful help he has given in the conduct of this experimental work.

SCIENTIFIC DEPARTMENT,
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X.—Preparation of Hyponitrite from Nitrite through Hydroxyamidosulphonate.

By Edward Divers, M.D., D.Sc., F.R.S., and TAMEMASA HAGA, D.Sc., F.C.S.

SULPHONATION, followed by hydrolysis, readily converts an alkali nitrite into the unstable hydroxyamidosulphonate, which, in a solution saturated with potassium hydroxide, has all its hydrogen replaced by

potassium, and is simultaneously resolved into hyponitrite and sulphite,

 $2\text{HO·NH·SO}_8\text{Na} + 4\text{KOH} = (\text{KON})_2 + 2\text{KNaSO}_8 + 4\text{H}_2\text{O}.$

This remarkable change was made known by us in 1889 (Trans., 1889, 55, 760), along with the fact that it afforded a rich source of hyponitrite, since the quantity of the latter formed is equivalent to at least half the nitrite taken. But this, it was pointed out, depended on our method of preparing hydroximidosulphonate being employed, and as the description of that method was not published until five years later, the new source of hyponitrite could not be used advantageously by others. Even since then, the method has escaped the notice of seven separate workers on hyponitrites, namely, Thum, W. Wislicenus, Paal and Kretschmer, Tanatar, D. H. Jackson, Piloty, and Hantzsch and Kaufmann, to be at last, however, taken up by Kirschner (Zeit. anorg. Chem., 1898, 16, 424). Indeed, it may be said to have been rediscovered by Piloty, who in a paper on "an oxidation of hydroxylamine by benzenesulphonic chloride" (Ber., 1896, 29, 1559), describes the resolution of benzenesulphonic hydroxylamide by potassium hydroxide into hyponitrite and benzenesulphinate, with a yield also of half the calculated quantity of the former salt.

As we have each of us very frequently employed the hydroxyamidosulphonate method of preparing hyponitrite, and the details requisite in order to get high yields have not been published, it seems it will be of service to chemists to describe the method fully.* So far as our experience goes, we can be certain of getting a yield of 60 per cent. of the theoretical, and occasionally much more, although we have not succeeded in discovering the cause of this. In what follows, we assume that the convenient quantity of 2 decigram-molecules of sodiumnitrite is taken, from which about 17 grams of silver hyponitrite may be obtained.

In order to limit the quantity of potassium hydroxide required, which is very large in any case, no more water than is necessary must be used, and except that particular attention must be given to this point, the process begins exactly like that of making hydroxylamine sulphate from nitrite (Trans., 1896, 69, 1665). In a tared, wide-mouthed, round-bottomed flask of 200—250 c.c. capacity, 14.4 grams of 96 per cent. sodium nitrite,† together with sodium carbonate containing 10.6 grams of anhydrous carbonate, are dissolved by heat in enough water to make the total weigh 83.5 grams. Some lead salt

^{*} Kirschner's method is an excellent form of our process, but I prefer that described in this paper.—E. D.

[†] But preferably, 18:8 grams of pure sodium nitrite, this being now very easy to prepare (this vol., p. 85).

in the nitrite is deposited, but goes into solution when the potassium hydroxide is added and gives no trouble. Sodium carbonate of any hydration may be used, but as, subsequently, more of this salt has to be added, and then should be approximately the monhydrate, it is convenient to use this form throughout. Such a carbonate, almost pure, is generally found in the "dried" pure carbonate of commerce. Keeping the flask in active motion in an ice-and-brine bath, sulphur dioxide is passed in until a short time after the temporarily precipitated acid carbonate has redissolved, and just when a bit of lacmoid paper in the solution becomes fully red. About 0.1 c.c. strong sulphuric acid is then dropped in. If the temperature is kept below 0°, the conversion of the nitrite into hydroximidosulphonate is complete, whereas if it rises much above 0° some nitrilosulphonate would form, and interfere with the result. If higher temperatures have been avoided, the nitrite and carbonate taken in molecular proportions, and the sulphur dioxide not used in excess, the solution is ready to be hydrolysed; but as the salts may not have been in exact proportion, and sulphur dioxide may also be present, it is best to blow a strong current of air through the solution at 0°, so as to expel any sulphur dioxide or nitric oxide that may be present.

After this treatment, the solution is brought to about 30°, in order to start hydrolysis, and set aside for a day in a warm place with the flask corked. Complete hydrolysis to hydroxyamidosulphonate without further hydrolysis to hydroxylamine is thus secured,* and, consequently, just the calculated quantity of sodium carbonate (10.8 grams anhydrous) is found to be required, including that for the three or four drops of sulphuric acid added. The approximately monhydrated carbonate, added in fine powder, is briskly shaken with the solution, so as to hinder its caking, the last portions being dissolved by warming the flask. The solution of hydroxyamidosulphonate and sulphate, thus prepared, contains almost exactly half its weight of water, is therefore supersaturated, and is the strongest solution practically obtainable; it will be found to approach closely 113 grams in weight, so smoothly do the reactions proceed. The solution may

^{*} That the production of hydroxylamine is avoided if this detail is attended to, has been proved by shaking the solution, after it has been made alkaline, with sodium amalgam, which readily converts hydroxylamine into ammonia, but does not act on the hydroxyamidosulphonate. On testing in this way, no odour of ammonia can be recognised, and moist red litmus paper held in the bottle is barely affected. Kirschner, using potassium hydroximidosulphonate, had to heat to boiling to effect hydrolysis, which is difficult then to complete without some of the hydroxyamidosulphonate passing on into hydroxylamine. When the hydrolysis is incomplete, nitrite will be regenerated later on by the alkali; and when it is carried too far, nitrite will also be formed during the oxidation of the hydroxylamine by the silver (or mercury) oxide.

be made weaker, and then concentrated, but the adjustment is troublesome, and the formation of hard cakes of sodium sulphate, which interferes with the proper working at the next stage of the operation, is difficult to avoid.

The contents of the flask are now well drained into a basin, preferably a hemispherical nickel basin, or, lacking that, a stout porcelain one, capable of holding about 500 c.c. Potassium hydroxide, free from chloride, assayed for real alkali and for water, and having not less than two-thirds and not more than 1 mol, of water to 1 of the hydroxide, is required, for if it were anhydrous it would cause much heating and consequent decomposition of the salts; generally, the potassium hydroxide purified by alcohol and the more translucent varieties of stick potash contain about the right proportion of water, and dissolve in water without much rise of temperature. From 130 to 165 grams of it, according to its degree of hydration, are quickly crushed in a warm mortar, thrown into the solution in the basin, and incorporated with it by means of a pestle. There is marked heating only just at first, which is better met by keeping the basin in water or resting it on snow or pounded ice for a very short time, stirring in the potassium hydroxide, the solution sets to a stiff paste. if kept cold, quickly becoming thin again on further stirring, but full of an opaque, white precipitate of sulphate. If the basin has been cooled, hardly any gas escapes at first, but gentle effervescence and much frothing occur before long in any case. When the potassium hydroxide has been all ground up and dissolved, the basin is placed under close cover from atmospheric moisture and carbonic acid, and left in a warm place for 30 hours; if kept for more than 50 hours, the quantity of hyponitrite sensibly, but slowly, diminishes. As much even as one-fourth of the hydroxyamidosulphonate may sometimes, in cold weather, still be present, and can be partly destroyed by keeping the basin at 55-60° for half an hour, although not with noticeable increase of the quantity of hyponitrite, but this heating, with the attendant risk of over-heating, is better omitted, on the whole. Besides undecomposed hydroxyamidosulphonate, the contents of the basin now consist of precipitated sulphate and sulphite, and solution of potassium hydroxide in slightly less than its weight of water (almost exactly KOH: 3H₂O), together with the potassium hyponitrite. It is, apparently, only to secure this concentration of the potassium hydroxide, a practically saturated solution, that hardly less than 10 mols. of it to 1 of hydroxyamidosulphonate have to be used. More of it may be added without effect, good or bad, unless the solution of the salts is weaker than is here recommended, for in that case additional potassium hydroxide must be used to bring the concentration to the right point.

Treatment with a silver salt is the only way of separating the hyponitrite from the other salts, and for this purpose the presence of the alkali is essential, together with large dilution when precipitating. The best way is to use the silver solution exceedingly dilute, because this checks the precipitation of silver oxide and sulphite until some time after all the hyponitrite has separated. Now the necessity for large dilution, and the advantage of still larger dilution, remove the only objection that can be raised to the use of silver sulphate instead of silver nitrate, and since it is generally important to feel assured that no trace of nitrate or nitrite can have been carried down with the hyponitrite, the sulphate should have the preference, although the nitrate can almost certainly be used with as good results. A cold saturated solution contains only 5 or 6 grams of the sulphate to the litre, and is most easily prepared by boiling excess of the salt with water and pouring the solution into an equal volume of cold water.

Whichever salt is used, the contents of the basin are first washed into a very capacious precipitating vessel, and the highly dilute silver solution is poured in until it ceases to produce any more black precipitate. When this is at all abundant, as it sometimes is in cold weather, an hour's interval is given for subsidence of most of it, the still dark solution is decanted, and the precipitate washed by decantation before rejecting it. With or without this interruption, the addition of the silver solution is continued until the bright yellow hyponitrite suddenly appears, and so long after as the joint precipitation of brown oxide can be easily checked by stirring. When the point is reached where the oxide only redissolves slowly and no longer gives place to a yellow one of hyponitrite, no more silver solution should be added. If much more were added, there would be permanent precipitation of silver oxide, which is apt to be accompanied by The quantity of silver sulphate required may be silver sulphite. as much us 40 grams, which means 7 or 8 litres of solution: if silver nitrate be used, about 44 grams will be wanted, dissolved in 4 litres, or more, of water.

Half-an-hour after precipitation, the solution is to be poured off, even though still a little turbid, and the precipitate washed by decantation, for there is a very slow deposition of a mirror of metallic silver from the sulphite solution, which goes on for days. In order to separate the hyponitrite from the metallic silver and its oxide, and perhaps chloride, it has to be dissolved in dilute acid and reprecipitated. If every trace of nitrite is to be kept out of the hyponitrite, nitric acid can hardly be used, because I find that it always contains some nitrous acid, and it is, therefore, necessary to use sulphuric acid. Since the hyponitrite must be kept in solution as ahort a time as possible, it is advisable to have the acid not very

dilute, in order to reduce the volume of liquid to be filtered. But high dilution is better, because the stability of hyponitrite falls off rapidly with increasing concentration; moreover, if the suphuric acid is not dilute enough, silver sulphate will separate; a 1 per cent. solution of the acid, well cooled in ice, is suitable, some 5 litres of it being required. The precipitate should be treated with the acid in portions at a time, not all together; and, as far as possible, the undissolved precipitate should be kept off the filter until the last. For so long a filtration a Lunge filter-tube-extension of the funnel is more suitable than the filter pump, the filtrate being allowed to fall directly into excess of sodium carbonate solution. Working with these precautions, the silver hyponitrite can be dissolved and reprecipitated, even in hot weather, with hardly any appreciable loss.

Having replaced the alkaline mother liquor by water, dilute sulphuric acid is cautiously added, until, after stirring up the precipitate well, the solution is no longer alkaline, and some of it, when filtered, is found to contain a trace of the silver hyponitrite; this is best ascertained by adding one or two drops of sodium carbonate solution to about 100 c.c. of it, which should cause a permanent, yellow, very slight, opalescence.

The precipitate, thoroughly washed by decantation and dried on a filter at the ordinary temperature in a desiccator, in the dark, and then at 100°, will give 78 per cent. silver (calc. 78.26). But in order to preserve the bright colour of the salt and its entire freedom from nitrite, all work on it should be done with very little exposure to bright daylight. The weight of silver hyponitrite obtained from the quantity of sodium nitrite employed should be not less than 17 grams.

IMPERIAL TOKYO UNIVERSITY, JAPAN.

XI.—Absorption of Nitric Oxide in Gas Analysis. By Edward Divers.

It is well known that the vapour tension of nitric oxide, dissolved in the solution of a ferrous salt, interferes with the use of this reagent to remove nitric oxide from other gases. There is, however, another absorbent for nitric oxide which leaves nothing to be desired, whose use and value have remained unknown. This is a strong solution of either sodium or potassium sulphite to which a little alkali hydroxide has been added. It quickly absorbs every trace of nitric oxide, which it fixes in the form of hyponitrososulphate, Na₂N₂O₂SO₃. I have

already made satisfactory use of it to analyse the mixture of nitric oxide and nitrogen which is left on heating silver hyponitrite and allowing the solid and gaseous products to cool in contact with each other. The sulphite need not be very pure, the presence of sulphate or carbonate being of no importance. If carbon dioxide or other acid gas is present along with the nitric oxide, it is removed by alkali before using the sulphite mixture.

XII.—Interaction of Nitric Oxide with Silver Nitrate.

By Edward Divers.

HAVING reason to think that silver nitrate might interact with nitric oxide if heated in it, and there being no information obtainable on this point, I have made some experiments on the action of nitric oxide on silver nitrate, as well as on other nitrates.

In the first place, something had to be ascertained as to the behaviour of silver nitrate when heated alone. Heated for 15 minutes in dry air or carbon dioxide, it suffers no chemical change until the temperature is close to the melting point of sulphur (444°), and the alight decomposition which occurs at that temperature, being accompanied by an action on the glass, may be due to that action. minute quantity of oxygen seems to be liberated, and there is a very slight greying of the faintly yellow liquid; on cooling and dissolving, there is slight turbidity from the presence of silver, and a trace of nitrite can be detected. Only at a much higher temperature does the salt decompose with free effervescence, and then nitric peroxide accompanies the oxygen, and silver is deposited; even then, nitrite is present in the mass only in very small quantity at any time, there never being enough to remain undissolved when the nitrate is treated with a little water. This is sufficient, however, to show that the primary decomposition of silver nitrate by heat alone is into silver nitrite and oxygen, the instability of silver nitrite at much lower temperatures, although diminished by the presence of nitrate (Trans., 1871, 24, 85), accounting fully for its being found in such small quantity when the temperature is high, and for the production of nitric peroxide and silver instead. As determined by Carnelley, the melting point of silver nitrate is 217°.

The nitric oxide used for the experiments was prepared by the ferrous sulphate method, stored for 2 days in a glass gas-holder, and dried in its passage to the silver nitrate by a sulphuric acid column. At starting, the air in the drying apparatus and in the tube containing

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the silver nitrate was expelled by carbon dioxide, the silver nitrate being heated in the gas, in order to dry it. Interaction between the silver nitrate and the nitric oxide was recognised by the reddening of the gas, and at the end of an experiment the gases were expelled by carbon dioxide before opening the tube.

Silver nitrate, when heated in nitric oxide, is strongly affected by it, being freely decomposed at a much lower temperature than that at which it decomposes when heated alone, the nitric oxide becoming oxidised. The action commences, perhaps, at 150°, but this is doubtful; at the melting point of the salt, it becomes marked, and at the boiling point of mercury considerable, but even at this temperature it is a long time before the decomposition is complete, the progress of the change gradually becoming slower. For some time, the products are silver nitrite and nitric peroxide, $AgNO_3 + NO = AgNO_2 + NO_2$, but very little silver is liberated, the nitrite being almost wholly preserved for a long time, through combination with the undecomposed nitrate. But when, as the nitrate becomes decomposed, the nitrite is no longer unprotected, it suffers decomposition, as usual, into silver and nitric peroxide; finally, nothing but silver remains.

Theoretically, it is quite probable that nitric oxide does not, after all, act directly on silver nitrate. For, making the allowable supposition that, to a minute extent, silver nitrate decomposes into silver nitrite and oxygen, at temperatures much below that at which it does so sensibly, the nitric oxide may be regarded as being active by combining with this oxygen, and thus, by removing it, greatly hastening the spontaneous decomposition of the nitrate. This decomposition, thus assisted, and occurring at temperatures at which silver nitrite is comparatively stable in presence of nitrate, the nitrite remains, although at higher temperatures it decomposes almost as fast as it is formed from the nitrate. According to this theory, silver nitrate is not actually decomposed by nitric oxide, but only decomposes much more rapidly in its presence, in consequence of its interaction with one of the products of decomposition. For practical purposes, silver nitrate and nitric oxide may, however, be treated as acting on each other when heated together.

Nitric oxide has no action on sodium potassium or barium nitrate, even at the temperature of boiling sulphur.

Lead nitrate soon begins to decompose by heat alone, and nitric oxide seems to be without effect on its decomposition. According to Stas, lead nitrate begins to decompose somewhere above 200°; I find that, for its fairly free decomposition, a temperature not much below 400° is required. At the boiling point of sulphur even, the decomposition proceeds at such a moderate rate that only after 10 minutes heating does the salt show distinct signs of fusing. No nitrite is pro-

duced, but a very little peroxide of lead is formed. By washing the mass with cold water, and then boiling it out with water, the beautiful, crystalline, white salt, Pb(OH)NO₂, can be obtained in abundance.

XIII.—Preparation of Pure Alkali Nitrites.

By EDWARD DIVERS.

When pure sodium or potassium nitrite is wanted, it is customary to prepare silver nitrite from crude alkali nitrite, and convert this again into alkali nitrite by means of sodium or potassium chloride. The crude nitrite must be nearly free from sulphate, and either before or after adding the silver nitrate to it, nitric acid must be added until all the hydroxide and carbonate are neutralised. The silver nitrite is got in the most convenient form for washing by precipitating it from concentrated solutions. Silver chloride is very sensibly soluble in a concentrated solution of alkali nitrite, and when the solution is no longer clouded by the addition of more alkali chloride, it already contains this salt in excess. Therefore, somewhat large dilution is necessary, and this entails, of course, much evaporation afterwards.

The silver nitrite process is evidently not a very satisfactory one, and when sodium nitrite is wanted pure, it is better to recrystallise, three times over, the commercial 96 per cent. sodium nitrite, well draining each time on the suction funnel. A concentrated solution of the crude salt should be left to clear from lead turbidity for two days, or be filtered cold through a fine filter; the lead carbonate is more soluble in the hot nitrite solution than in the cold. After separating the lead, the solution should be fully neutralised with nitric acid before evaporation for crystallising. Potassium nitrite is too soluble and deliquescent to be conveniently purified in a similar way.

A most satisfactory and simple process for preparing either sodium or potassium nitrite, when the pure hydroxide or carbonate is at command, is to saturate this with red nitrous fumes under appropriate conditions. That nitrites can be thus obtained is known to every chemist, was known to Gay-Lussac in 1816, and was described by Fritzsche in 1840, but it has hitherto been stated and believed that much nitrate is then unavoidably formed along with the nitrite. That is a mistake, and therefore this note is published. If obvious precautions of the simplest kind are taken, so little nitrate, if any, is formed as to be hardly detectable with certainty in presence of so much nitrite. Consequently, if the quantity of pure alkali taken is known, a solution of given strength in nitrite is perhaps better prepared in this way than in any other.

Avoiding, so far as practicable, the use of cork and caoutchouc, nitrous gases, from nitric acid and starch or arsenious oxide, are passed into the concentrated solution of the hydroxide or carbonate until the alkali is quite neutralised. Sodium carbonate alone is somewhat inconvenient, because of its sparing solubility, but this may be circumvented by adding it, finely divided and in sufficient quantity, to its own saturated solution, just before passing the gases and by often shaking the vessel during their absorption. To prevent free access of air, the nitrite is prepared in a flask with its mouth kept loosely closed while the gases are passing; it is not necessary to cool the flask. The strength of the nitric acid and the temperature of the generator of the nitrous gases must be so regulated that just a little nitric oxide is in excess of the nitric peroxide, and therefore is passing unabsorbed, as a guarantee that the latter does not act on the solution in absence of its equivalent of the former and thus produce some nitrate. To free the gases from volatilised nitric acid, they may be passed through a bottle or tube, either empty or packed loosely with cotton. The finished solution must be almost neutral, and if acid must be boiled until neutral, before exposing it to the air. A concentrated solution of alkali nitrite dissolves a little nitrous acid without decomposing it, as water alone would. To get the salt in the solid state or to crystallise out the sodium nitrite where it is necessary to be sure of absence of all nitrate in it, the solution may be freely evaporated, even at a boiling heat, without decomposing or oxidising it.

The alkali nitrites have been very imperfectly described, and need In the meantime, some points in their description are examination. here given. Sodium nitrite and potassium nitrites are distinctly though faintly yellow, and give markedly yellow solutions in a little water. They are very slightly alkaline to litmus. At 15°, 5 parts of sodium nitrite requires 6 parts of water to dissolve it; potassium nitrite is soluble in about one-third of its weight of water. Sodium nitrite melts at 271° (mercury-thread immersed). Sodium nitrite is moderately deliquescent, remaining dry in winter-cold air; potassium nitrite is exceedingly deliquescent, and is obtained in very small. thick, prismatic crystals, whilst sodium nitrite crystallises in very thin, flattened prisms, often very large. Sodium nitrite is well known to be anhydrous; not so potassium nitrite, crystals of which are reputed to contain $\frac{1}{2}H_0O$. I have, however, examined small, but distinct and separate, crystals taken from the upper part of some kilos. of the commercial salt, which had become well drained by long standing. They were removed in very dry weather and weighed, and then found to lose hardly 1 per cent. on fusion. The anhydrous character of the potassium salt was further ascertained by testing a cake of minute crystals, prepared by myself, which had been pressed,

under cover, between porous tiles, in cold, dry air; the loss of weight on heating, much above 100°, was a little over 1 per cent., and the percentage of potassium was 45.30, instead of 45.88, required for the anhydrous salt.

Somewhat remarkably, the point as to hydration of potassium nitrite was examined independently in the same year, 1863, by Lang and by Hampe, with identical results, indicating the composition expressed by $2KNO_2 + H_2O$, but both these chemists made the determination on a magma of indistinct crystals, which had been dried in a vacuum desiccator.

XIV.—Reduction of an Alkali Nitrite by an Alkali Metal.

By Edward Divers, M.D., D.Sc., F.R.S.

It is already known what are the products which may result from the action of sodium amalgam on a solution of sodium nitrate or nitrite. Schonbein (1861) first observed the formation of nitrite by the action of metallic sodium on a solution of a nitrate; and de Wilde (1863) that nitrous oxide, nitrogen, and ammonia are the products of the action of sodium amalgam on a solution of potassium, sodium, or ammonium nitrate, or on potassium nitrite; he found that, except alkali hydroxide, nothing else is produced, and, in particular, no hydrogen. Some years later (1870), however, it was recognised by Fremy, aided by a suggestion of Maumene's, that hydroxylamine, or what appeared to be hydroxylamine, was a product of the reduction. Then came (1871) my own discovery of the hyponitrites, together with the observation that alkali nitrates in solution are largely convertible into nitrites by sodium amalgam, an extension of Schonbein's experience. Lastly, Haga and I (1896) proved that the actively reducing substance observed by Fremy is actually hydroxylamine, as it had been taken to be by Maumené and by him, and not hydrazine, as it might have been. By a mistake, already pointed out and corrected by me (Annalen, 1897, 295, 366), the discovery of the hyponitrites has been in recent years attributed to Maumené. It will suffice here to say that this veteran French chemist has, it so happens, published, in another connection, that he had not experimentally investigated the reduction of nitrites in solution, and that, far from laying claim to the discovery of hyponitrites, he at first denied its truth on theoretical grounds (Trans., 1872, 25, 772; Chem. News, 25, 153 and 285).

Nitrous oxide, nitrogen, hydroxylamine, ammonia, sodium hyponitrite, and sodium hydroxide (from the nitrite as well as from the

metal), are, according to my experience, always produced in the reduction of sodium nitrite or nitrate by sodium amalgam, but in proportions which vary greatly within well-marked limits. Nearly one-sixth of the nitrogen can be obtained as sodium hyponitrite in one way of working, or scarcely any at all in another. So, too, the range of production of hydroxylamine is from nearly 9 per cent. of the nitrogen of the nitrite down to one-third per cent. The presence of ammonia may be very strongly manifest, or be hardly perceptible and escape notice. The two gases, nitrous oxide and nitrogen, together represent at least 80 per cent. of the total nitrogen, and may vary in relative proportion to the extent of either of them being nearly absent. Necessarily, all the sodium of the nitrate or nitrite, not left as hyponitrite, appears as hydroxide, along with that derived from the metallic sodium used as the reducing agent. So long as any nitrite remains, hydrogen does not occur among the products, unless a very large quantity of water is present, whilst, if there is very little water, hydrogen is not evolved even after all the nitrite is gone.

Within the limits indicated, the proportioning of the products of the reduction is well under control. The concentration of the solution of nitrite, or, to put it better, the relative quantity of water present, exercises most influence, the only other circumstance affecting the course of the reduction being the temperature. The concentration of the sodium in the amalgam and the proportions of the sodium and the nitrite have no direct effect on the reduction. Working with a sufficiently concentrated solution of nitrite, the proportions of the products remain constant throughout the reduction of the nitrite. Probably this is the case also when an exceedingly dilute solution is used; but with a somewhat dilute solution, say 1 in 30. there is some difference, due to the fact that the presence or absence of much sodium hydroxide modifies the proportions of the products, and that this substance is generated so largely. A dilute solution of sodium nitrite may be made to behave as a concentrated solution in the mode of its reduction by nearly saturating it with sodium hydroxide before bringing it in contact with the sodium amalgam; but the addition of sodium hydroxide to a concentrated solution of nitrite before reducing it by the amalgam has no sensible effect, for the reason, no doubt, that, in the reduction of the nitrite as it actually occurs, about 31 mols. of sodium hydroxide are produced for 1 mol. of nitrite reduced, quite enough, therefore, of itself to make the water of a concentrated solution almost proof against the action of sodium. With a large quantity of water present, the sodium hydroxide formed is not enough to render the water inactive, and in this is to be found the explanation of the great difference observed in the proportions of

the products, according as the nitrite is dissolved in much or little water.

In order to produce as much hyponitrite as possible, little more is necessary than to work with a concentrated solution of the nitrite (1 of sodium nitrite to 3 or $3\frac{1}{2}$ water), to add the amalgam in some excess, and not to allow the temperature to rise above 100° . To get as much hydroxylamine as possible, the solution of nitrite must be dilute (say 1 in 50), and be kept cold during the addition of the amalgam. To preserve the hydroxylamine from reduction to ammonia, the solution must be kept well agitated over the amalgam, and be poured off from it as soon as nearly all the nitrite has been reduced. Much more time is needed to reduce a dilute solution than a concentrated one. The best conditions for producing much hydroxylamine do not allow of much more than half the maximum yield of hyponitrite being obtained at the same time.

To get much nitrous oxide, the temperature of the solution must be kept as low as possible, whilst to get much nitrogen, the temperature must be kept high, the strength of the solution of nitrite being without effect. The reduction of a very dilute solution of sodium nitrite kept very cold is attended with very little effervescence. because the quantity of nitrogen produced is very small and the nitrous oxide remains dissolved, although it is readily evolved on warming. De Wilde has determined the proportions of the gases to each other, but only when the nitrite (or nitrate) was in excess of the sodium; that however, is sufficient, since qualitative examination of the gases has shown me that variations in the proportions of salt and metal are without sensible influence on the composition of the gases, and also that this remains apparently unchanged during the progress of the reduction if the temperature is kept tolerably uniform. De Wilde found that dilute solutions of nitrite or nitrate of sodium or potassium gave larger quantities of nitrous oxide in proportion to nitrogen when the solutions were dilute than when they were concentrated, from which it might seem that the strength of the solution does affect the proportions of the gases to each other; but in the experiments conducted by de Wilde, the much greater rise of temperature when concentrated solutions are acted on fully accounts for the results he obtained.

Ammonia can always be detected from the beginning of the reduction (Thum thought not), but its amount may be minute throughout. It can be got in considerable quantity by using a cold dilute solution, as for producing hydroxylamine, and, after the main action is over, shaking it with amalgam in a stoppered bottle until all the hydroxylamine has disappeared. It can also be got somewhat concentrated for a short time by dropping the concentrated solution of the nitrite on

to much solid sodium amalgam, as was first observed by de Wilde but even then much hyponitrite is produced. Very hot and dilute solutions of nitrite treated with sodium amalgam give little else than ammonia and nitrogen.

The reduction of potassium nitrite by potassium amalgam closely resembles that of the sodium salt by sodium amalgam, in every respect, both quantitative and qualitative.

If, for the moment, nitrogen and hydroxylamine be disregarded, as they well may be, since their proportions become very small under suitable circumstances, the nitrite may then be said to be reduced simply to hyponitrite and much of this hydrolysed into nitrous oxide and sodium hydroxide. This, at one time, I, as well as other chemists, supposed to be the case. But, for a long time now, I have felt that most of the nitrous oxide and sodium hydroxide must have another origin. Thum has expressed himself in the same sense, basing his opinion upon the comparative stability of sodium hyponitrite in strongly alkaline solution, for it is only gradually decomposed even when boiled with it. This fact by itself, however, is not inconsistent with the assumption that the nitrous oxide and sodium hydroxide represent decomposed hyponitrite. But it does not stand alone; for (a) Hot concentrated solutions of nitrite yield quite as much hyponitrite as cold ones, unless the temperature is well above 100°. and even then the yield does not fall off much. (b) In all cases, the effervescence accompanying the formation of hyponitrite goes on exclusively at the surface of contact with the amalgam. (c) Low production of hyponitrite is not attended with higher production of nitrous oxide. All these facts are opposed to the view that the nitrite is all reduced to hyponitrite in the first place; so, too, is what follows.

Although the proportions of the products of the reduction of the nitrite vary greatly with the circumstances, it is only within wellmarked limits; thus, of the nitrite reduced there is from a sixth, under one set of conditions, to almost a fifth, under other conditions, which becomes partly hyponitrite and partly hydroxylamine (and ammonia), whilst the rest becomes nitrogen and nitrous oxide, one or the other predominating, according to circumstances. So, too, in one extreme case, nearly all of the one-sixth of the nitrite will change into hyponitrite, very little becoming hydroxylamine; or, on the other hand, of nearly one-fifth of the nitrite more than half may be converted into hydroxylamine, only the rest of the fifth becoming hyponitrite. It may, therefore, safely be assumed that about onefifth of the nitrite tends to, or is able to, become hyponitrite. although barely one-sixth of the nitrate can yet be secured as this salt, because either some of this fifth becomes hydroxylamine, or else a little of the hyponitrite is hydrolysed at once or during the

process of isolating it. With that assumption to give more precision to the statement, it may be affirmed that many experiments under varied conditions have shown that about a fifth of the nitrite is decomposed by sodium amalgam in one way, and four-fifths in another way; in the one, hyponitrite, hydroxylamine, and alkali (with a very little ammonia and nitrous oxide as secondary products) are formed, and in the other, nitrogen, nitrous oxide, and alkali; so that when much hydroxylamine is formed it is at the expense of hyponitrite only, and when much nitrogen is produced it is at the expense of the nitrous oxide only.

But although this is the case, the hydroxylamine does not seem to be derived from the hyponitrite, or the nitrogen from the nitrous oxide, but, rather, the one pair of substances is derived from one transition product, and the other pair from another transition product. It was pointed out in my first paper that sodium amalgam does not act on hyponitrite, and this has since been more fully established by Dunstan and Dymond, and again by Thum; according to the last-named chemist, hyponitrous acid is not reduced even by zinc and boiling dilute sulphuric acid. In confirmation of my earlier statement, I can now assert that sodium amalgam has no action whatever on a solution of sodium hyponitrite saturated with sodium hydroxide, even at 80° (and, no doubt, at higher temperatures), and when in contact with it for days together; no hydroxylamine, ammonia, nitrogen, or hydrogen is produced. In weaker alkaline solutions, hydrogen is very slowly evolved, but still without the hyponitrite being affected. Weak alkaline solutions of sodium hyponitrite, however, slowly decompose of themselves, and then some of the nitrous oxide may possibly get reduced by the sodium amalgam.

As for the nitrogen, it is evident that only while nitrous oxide remains in solution and comes in contact with the amalgam can it be reduced, even if it is then (see p. 95). Yet, in order to get much nitrogen in place of nitrous oxide, it is necessary to work with hot solutions, when the solubility of nitrous oxide is at its lowest. It is not essential that the quantity of nitrite should be small in proportion to the sodium, temperature alone appears to be the condition determining the formation of nitrogen in place of nitrous oxide. In other words, weak solutions of nitrite and excess of amalgam in no degree favour the production of nitrogen rather than of nitrous oxide, and the proportion of nitrogen is not greater in the gases escaping towards the end of a reduction than at the beginning.

Very different is it with ammonia, which is truly a product of the reduction of hydroxylamine (in non-acid solution), and the formation of which takes place principally during the final action of the amalgam. Against the notion, highly improbable as it is, that the

nitrogen may come from yet undecomposed nitrite and already formed ammonia, which would also account for the comparative absence of ammonia in the earlier part of the reduction, there may be adduced de Wilde's observation, that ammonium nitrate, when reduced by sodium amalgam, gives much more nitrous oxide in proportion to nitrogen than potassium or sodium nitrate does, no doubt because there is less rise in temperature.

Without speculating on the constitution of a nitrite, we are able to see from the interactions between ethylic iodide and silver nitrite that a nitrite may react both as an oxylic salt, NaONO, and as a halide, NaNO₂. From the reduction by sodium there will then first result the radicles NaON= and NaNO; from the former, or sodoximido-radicle, may well come the hyponitrite and hydroxylamine, and from the other, or sodium nitroside radicle, the nitrous oxide and nitrogen. In accordance with the facts observed, the sodoximide, in concentrated alkaline solution, will condense to sodium hyponitrite, stable against reduction, or, in very dilute alkaline solution, will, by hydrolysis and reduction, become alkali and hydroxylamine. The hypothetical nitroside will also condense and simply hydrolyse into nitrous oxide and alkali, mainly at low temperatures, or will become reduced and hydrolysed into nitrogen and alkali, principally at higher temperatures.

To establish the points in the reduction of the two nitrites by their respective metals, here described, I have made very many experiments, usually working on quarter-gram molecules of nitrite. The hyponitrite obtained was weighed as silver salt. The hydroxylamine was estimated by the quantity of metallic silver it yielded, and in this way: the black precipitate it causes in silver nitrate solution, in presence of alkali, being largely suboxide, was washed with cold dilute nitric acid and ammonia alternately, and the residual brownish metallic silver weighed and calculated into hydroxylamine by the ratio $2Ag: NH_3O$, experiments (described in the next paragraph) with solution of hydroxylamine sulphate of similar dilution and alkalinity having shown that this could be done accurately enough.

The important observation, made by Thum, that hydroxylamine, when oxidised by suitably alkalised mercuric oxide, silver oxide, or cupric hydroxide, will yield a little hyponitrite and nitrite, induced me to ascertain whether, in my experiments, the destruction of hydroxylamine in this way, sometimes in considerable quantity, might not account for some of the hyponitrite afterwards found to be present. To ascertain whether this took place, I made a blank experiment very similar to those made in studying the reduction of sodium nitrite, except that sodium hyponitrite itself was absent. Thus, hydroxyl-

amine sulphate, 1.5 grams (= 0.6 gram hydroxylamine) was dissolved along with 32 grams of sodium hydroxide in nearly 2 litres of water, and then a solution was run in, with stirring, of 7.5 grams of silver nitrate. which was a considerable excess, such as was used in the other experiments. The abundant, black precipitate was washed, exhausted with ice cold, dilute nitric acid, and the solution, neutralised as usual in my other experiments, gave no silver reaction for silver hyponitrite, and nothing more than a slow and very slight action on permanganic acid, which might be due to a trace of either nitrous or hyponitrous acid. It was easily seen that some nitrous acid was formed, by applying the iodide and starch test. Under the circumstances of my experiments, therefore, even when 7 per cent. of the nitrite had been reduced to hydroxylamine, there could have been no perceptible production of hyponitrite during the after oxidation of the hydroxylamine. The metallic silver, washed out with dilute nitric acid and ammonia, weighed 3.8 grams, the calculated quantity being 3.95 grams. nitrite detected in the mother liquor of the black precipitate had been formed in too small a quantity to materially affect the weight of the metallic silver.

Generally, sodium hydroxide was approximately estimated, after all the hyponitrite had been precipitated, by titration of the mother liquor with nitric acid, and of the silver oxide that had been precipitated along with the silver hyponitrite and the metallic silver. The amalgam used was of approximately known strength, ascertained, not by sampling, which is impracticable, but by uniformly preparing successive quantities, and sacrificing one to assay by dilute sulphuric acid and weighing the sodium as sulphate; after use in reducing nitrite, the sodium remaining in the mercury was sometimes determined in the same way. Nitrous oxide and nitrogen were not measured; their total nitrogen was found by difference, and their proportions had been sufficiently ascertained by de Wilde, as I have already said; but their relative abundance was estimated by a burning splint of wood, the reduction of the nitrite being always conducted in a loosely closed flask. The range of this reaction was from that of a gas utterly extinguishing combustion to that of one which supported it most vividly; in any uniformly conducted experiment, the gases evolved towards the end behaved like those given off at first.

To ascertain the effect on its reduction by sodium of adding sodium

It was proved many years ago that silver is insoluble in dilute nitric acid, the presence of nitrous acid being necessary to make it dissolve. But the contrary has been since asserted to be true where the silver is finely divided, as when precipitated. This error, as I must regard it, is due to precipitated silver when black or blackish containing suboxide, which gives it its colour: this is resolved by acids into oxide of silver, which dissolves, and metallic silver, which is left.

hydroxide to a concentrated solution of sodium nitrite (negative as this proved to be), two methods were adopted. In one, the amalgam was covered with a cold saturated solution of sodium hydroxide, which has no action on it, and then the concentrated solution of nitrite was slowly added; at first, the alkali greatly impedes the action of the amalgam on the nitrite, but when more of the solution of the latter is added, the action goes on faster and to the end, and gives the usual large proportion of hyponitrite with very little hydroxylamine. In the other, a concentrated solution of sodium nitrite and sodium hydroxide was treated with some of the amalgam; then more sodium nitrite was added, and then more amalgam. The result was the same as before. The object of working in this way was to obtain the effect, if any, of the most concentrated alkali from the first, without having to deal afterwards with a very large excess of alkali when the analysis had to be made.

I have also tried to ascertain the effect of diminishing the amount of alkali present. In acid reducing mixtures, nitrous acid becomes largely converted into hydroxylamine without production of hyponitrous acid, so that it seems probable that, could the alkali formed in the reduction of the nitrite by sodium be neutralised nearly as fast as it is produced, much hydroxylamine would be obtained and very little hyponitrite. The use of the ordinary acids for the purpose in such a way as to give conclusive evidence on the point does not seem to be practicable, whilst the great rapidity of the process of reduction makes the use of carbon dioxide (Aschan, Ber., 1891, 24, 1865) very unpromising. I have, therefore, tried the effect of adding ammonium acid carbonate along with the sodium nitrite, expecting the ammonia to be inactive. In one case, where I used the amalgam in large excess, much ammonium amalgam was formed, and, what was quite unexpected, neither hyponitrite nor hydroxylamine. In another experiment, in which the nitrite was kept in excess of the amalgam, the previous addition of the ammonium carbonate in excess was without any effect; the nitrite solution had to be used slightly dilute because of the carbonate, and gave, therefore, a little less hyponitrite (about 12.7 per cent. of the nitrite consumed) and a little more hydroxylamine (about 3 per cent.) than in the best way of working for hyponitrite. The presence of the ammonium carbonate was, therefore, without effect, the reaction between the nitrite and the sodium being already complete when the sodium oxide comes in contact with the water and ammonium carbonate.

I satisfied myself that a fairly concentrated solution of nitrite is uniformly reduced from the commencement to the end of the reaction if the temperature is kept tolerably constant, the method employed being to examine the gases in the way described, and the hyponitrite

and hydroxylamine as follows. To a solution of nitrite, one-half only of the quantity of sodium amalgam required to reduce it was added, and it was then found to contain hyponitrite and hydroxylamine in the same relative proportion as if the nitrite had been fully reduced (with cooling), and in approximately half the quantities the nitrite would have yielded if the full amount of sodium amalgam had been added.

Sodium amalgam was proved to have little or no action on nitrous oxide by exposing the gas for a long time to its action. The amalgam was liquid, and, when shaken up with the moist nitrous oxide in a stoppered bottle, coated the sides of the bottle. With occasional vigorous shaking, the bottle was kept closed four days; when opened, it was found to contain the nitrous oxide little, if at all, deteriorated In another similar experiment, a as a supporter of combustion. saturated solution of sodium hydroxide was poured over the amalgam; in this case, the amalgam did not coat the sides of the bottle, but the solution served to keep the dissolved nitrous oxide in contact with the amalgam. The bottle was often vigorously shaken, and was not opened until after four days. The nitrous oxide was almost or quite unchanged. Holt and Sims have studied the oxidation of sodium and potassium by nitrous oxide, but only at much higher temperatures than those in these experiments, which were at 25-30°.

IMPERIAL TOKYO UNIVERSITY, JAPAN.

XV.—Hyponitrites; their Properties, and their Preparation by Sodium or Potassium.

By Edward Divers, M.D., D.Sc., F.R.S.

The hyponitrites have received the attention of many chemists besides myself since their discovery in 1871, and even this year new ways of forming them and the new working of an old method have been published. Yet much has been left to be put on record before a fairly correct and full history of these salts can be said to have been given, and the present paper is meant to be the necessary supplement to what has already been published.

Ways of forming Hyponitrites.

No writer on hyponitrites in recent years has shown himself acquainted with all the known ways of getting these salts, or even with the most productive. The following complete list is valuable, therefore, and is of special interest as bringing together the various modes of formation of these salts.

- 1. Reduction of an alkali nitrite by the amalgam of its metal (Divers, 1871).
- 2. Reduction of an alkali nitrite by ferrous hydroxide (Zorn, 1882; Dunstan and Dymond).
- 3. Reduction of (hypo)nitrososulphates by sodium amalgam (Divers and Haga, 1885).
- 4. Reduction of nitric oxide by alkali stannite (Divers and Haga, 1885).
- 5. Reduction of nitric oxide by ferrous hydroxide (Dunstan and Dymond, 1887).
- 6. Decomposition of a hydroxyamidosulphonate by alkali (Divers and Haga, 1889).
- 7. Oxidation of hydroxylamine by sodium hypobromite (Kolotow, 1890).
- 8. Oxidation of hydroxylamine by mercuric oxide, silver oxide, or cupric hydroxide (Thum, 1893).
- 9. Interaction of hydroxylamine and nitrous acid (Thum, H. Wislicenus, Paal and Kretschmer, Tanatar, 1893).
- 10. Oxidation of hydroxylamine by benzenesulphonic chloride and alkali (Piloty, 1896).
- 11. Interaction, in methylic alcohol, of hydroxylamine with nitrous gases (Kaufmann, 1898, *Annalen*, 299, 98).
- 12. Interaction, in methylic alcohol, of hydroxycarbamide and nitrous gases (Hantzsch, 1898).
- 13. Interaction of dimethylhydroxynitrosocarbamide and alkali (Hantzsch and Sauer, 1898).

Menke's reduction of fused alkali nitrate by iron, and Rây's reduction of mercuric nitrite by potassium cyanide in solution, are not included in the list, because both reductions are very doubtful, and require confirmation before they can be accepted. In the present paper, only the original method of preparing hyponitrites will be treated of.

Preparation of Sodium Hyponitrite Solution by the Reduction of Sodium Nitrite with Sodium Amalgam.

Sodium nitrite can be converted by sodium amalgam in the easiest and quickest imaginable way into fully one-sixth of its equivalent of sodium hyponitrite; this remains in solution, and is pure but for the presence of much sodium hydroxide. From this solution, the sodium salt itself, as well as silver hyponitrite, can be at once prepared, nearly pure and with hardly any loss. The solution, if

cautiously neutralised, is also at once fit for preparing lead, copper, mercury, and some other salts. The neutralisation is known to be complete when a little of, the solution just ceases to give black oxide when mixed with a drop of a dilute solution of mercurous nitrate. Others who have tried this method, and particularly Hantzsch and Kaufmann, got far less favourable results.

Pure sodium nitrite is necessary, but that can now be prepared very simply (this vol., p. 85). In order to get as much hyponitrite as possible and as little hydroxylamine, the nitrite must be in concentrated solution; three times its weight of water seems to be the best quantity to dissolve it in when operating in the way to be described. Using these proportions, there is enough water to form, with the sodium oxide produced, a solution of the composition NaOH+3H₂O, which is a nearly saturated solution of NaOH,H₂O at the mean temperature. In presence of so much hydroxide, the water is also quite saturated with hyponitrite, a small quantity of this salt even separating when the solution is kept at 0° for a time.

To reduce sodium nitrite in cold concentrated solution, 21 atoms of sodium are needed, the additional half atom being consumed in the unavoidable formation of some nitrogen, hydroxylamine, and ammonia. This accords well enough with the statement in my first paper, as a first approximation, that not more than 4 atoms are active on sodium nitrate. In practice, however, 3 atoms of sodium should be used in reducing sodium nitrite, partly because it is wanted afterwards to reduce hydroxylamine, and partly because it is important that all the nitrite should be reduced, and this, notwithstanding statements to the contrary, can only be accomplished quickly in presence of a good excess of sodium. The strength of the amalgam is not an essential point; I have, however, found it most convenient to work with a soft, solid amalgam having the composition (NaHge) or 23 grams of sodium to 1600 grams of mercury.† The temperature, also, is not of importance if only the solution of nitrite is concentrated, and although it may in fact rise nearly to 100° without harm, it is better to follow my original direction to keep the flack in a stream of cold water during the reduction. It is, however, preferable to cool it, particularly in warm weather, by means of a brine and ice bath, as then the amalgam can be added much faster without producing any great evaporation. The temperature of the solution during the reduction then ranges, with a convenient rate of

^{*} Sodium hydroxide forms a saturated solution at 15° in its own weight of water. When cooled, this solution deposits large pointed prisms of the monhydrate.

[†] Tanatar erred in supposing that I recommended the use of hard amalgam, and his supposed improvement of my process is not one in fact.

working, from 5° to 25°, and the time taken to add 23 grams of sodium need not be more than 10 minutes.

From a quarter to a half gram-molecule of sodium nitrite is a convenient quantity to work on, and the solution is best contained in a 350 to 450 c.c. pear-shaped, wide mouthed flask, lying very obliquely in the cooling bath while the amalgam is added by means of a spatula. The last fourth of the amalgam may be put into the flask as rapidly as it can be, and the flask may then be removed from the bath. It is kept actively rotated for 10-15 minutes, during which the temperature will rise to about 40° and then fall. The solution and mercury are next poured into a narrow mouthed stoppered bottle so as to half fill it, the thick, aqueous solution adhering to the flask being washed into the bottle, but the water used should be limited to 2 or 3 c.c. if it is desired to obtain the solid sodium salt. is now violently shaken for 10 minutes or so, so as to destroy all the hydroxylamine. To ascertain this, a drop of the solution is tested by diluting it and adding a drop of silver nitrate solution, and a slight excess of dilute nitric acid; there should not be the slightest black tint due to silver reduced by hydroxylamine. No gas is liberated during the shaking, but a very strong odour of ammonia is developed. Strange to say, a minute quantity of nitrite is still present, and it seems almost impossible to entirely remove it, although it can be so far reduced by an hour's shaking of the solution with the amalgam that the acidified solution does not blue potassium iodide and starch until it has stood for about an hour.

On separating the solution from the amalgam and exposing it in a dish overnight over sulphuric acid, under reduced pressure, it will be free from ammonia, and is virtually a pure and stable concentrated solution of sodium hyponitrite and hydroxide.

As here described, the preparation of a solution of sodium hyponitrite ready for use is the same as that followed by me in 1871 (with nitrate), except the important modification in the manner of removing the hydroxylamine. When silver hyponitrite is prepared from the crude solution, the hydroxylamine gets destroyed by silver oxide, as I pointed out in the addendum to my first paper. Zorn, as an improvement, introduced the use of mercuric oxide, on the ground that destruction of some silver hyponitrite was thus avoided, but he overlooked the fact that it is the silver oxide, just as it is mercuric oxide, which becomes decomposed, the hyponitrite or any other acid radicle being untouched by the hydroxylamine in alkaline solution. Whether, therefore, mercuric oxide, or silver nitrate, or mercuric nitrate is used, and the precipitated metal then separated, the result is just the same in concentrated alkaline solutions, except that the dropping in a solution of the nitrate is more easy to carry out

than stirring up with mercuric oxide. Further, where the alkaline solution is very weak, the use of mercury compounds is not without objection, as a little mercuric oxide remains in solution. But whether silver or mercury oxide is employed, the result is unsatisfactory, for, as Thum has pointed out, both these oxides, in destroying the hydroxylamine, regenerate nitrite. Not, however, that Thum himself found this prevented him from successfully purifying the silver hyponitrite from nitrite by thorough washing and reprecipitation. thelot and Ogier, Paal and Kretschmer, and I myself, have not, however, met with the same success, as I found it necessary, in order to get silver hyponitrite free from all trace of nitrite, to begin by precipitating it in the absence of nitrite. Nevertheless, far from casting doubt on Thum's statement, I believe his silver salt to have been some of the purest ever prepared, from the account he has given of the properties of hyponitrous acid. No one, however, will be disposed to deny the superiority of sodium as a means of removing the hydroxylamine from the solution.

An almost pure solution of sodium hyponitrite can be conveniently got by dissolving the freshly prepared, hydrated, solid salt in water. Sodium iodide, or potassium iodide and the silver salt, will also furnish a solution of alkali hyponitrite. To get a solution for precipitating purposes, Thum proceeded in an indirect way, first preparing a solution of hyponitrous acid, and then adding enough sodium hydroxide to make the solution neutral to phenolphthalein, an effective but very wasteful process. Kirschner also, wanting a solution for precipitating purposes, used sodium chloride and silver hyponitrite, which, in complex and wasteful way, he made to yield a solution which although mixed with much chloride and nitrate, was practically free from silver.

Sodium Hyponitrite.

In 1878, Menke gave full analyses of crystals of a stable salt having the composition of sodium hyponitrite containing $6\mathrm{H}_2\mathrm{O}$, which he had prepared by deflagrating in an iron crucible a mixture of sodium nitrate and iron filings, keeping the product at a red heat for an hour in a fire of charcoal rather than of gas, boiling the mass with water, filtering off iron oxide, evaporating, and leaving to crystallise. He makes no reference in his paper to the large amount of sodium hydroxide he must have had to deal with, although this should have seriously affected the procedure. In 1882, Zorn submitted Menke's method to a thorough examination, but failed to obtain the least trace of hyponitrite; he found, however, that ferrous hydroxide, acting on a solution of sodium nitrite, did produce sodium hyponitrite (in solution). His suggestion that Menke had mistaken

carbonate for hyponitrite takes no account of the fact that the nitrogen and water in the salt were repeatedly determined. It can now, however, be stated with certainty that Menke's salt was not the sodium hyponitrite obtainable by reducing sodium nitrite by sodium amalgam and water, for this differs from it in degree of hydration, stability, and in other properties.

D. H. Jackson (Proc., 1893) described two ways in which he had succeeded in preparing sodium hyponitrite, but with such difficulty that he was deterred from investigating its properties; indeed, he merely mentions, in proof of his success, that he obtained crystals which contained the theoretical proportion of sodium, but this happens to be no proof at all, as sodium carbonate has just the same content of sodium; moreover, the hyponitrite is a hydrated salt which cannot be rendered anhydrous without some decomposition, and although of crystalline texture, the salt can hardly be described as occurring in crystals. Nevertheless, his success in getting the salt is not to be doubted. One of the methods he adopted was to reduce a concentrated solution of sodium nitrate by sodium amalgam, evaporate the solution in a vacuum until the salt crystallised, and wash the crystals with alcohol to free them from sodium hydroxide. With some modification, the process he followed is an excellent one.

To obtain sodium hyponitrite from the somewhat thick solution preprepared as already described, it is first passed through a Gooch asbestos filter well covered from the air; it contains 1 mol. of sodium hydroxide to 3 mols. of water, and is a saturated solution of the hydroxide, whilst there are about 211 atoms of sodium present as hydroxide to 1 as hyponitrite. Cooling alone will cause the separation of the hyponitrite, and the solution readily loses water in a vacuum over sulphuric acid until it retains only about 2 mols. to 1 mol. sodium hydroxide, when almost the whole of the sodium hyponitrite will have separated; at 25-30°, this will happen in about 40 hours, the salt separating as minute, crystalline granules, some of which adhere to the walls of the dish, but most of them being deposited as a thick crust on the surface of the solution. Below 15°, the mother liquor readily deposits crystals of the monhydrate of sodium hydroxide, and as evaporation is slower in the cold, it is better, for both reasons, to conduct the operation in a warm room.

The only effective way of separating the salt from its viscid mother liquor is by the pump and a Gooch crucible unlined with asbestos; draining on a tile is impossible. In the same apparatus, it is washed with absolute alcohol and then transferred to a basin and gently triturated with fresh portions of alcohol until all the sodium hydroxide has been removed. If now drained on a good tile, it is the nearly pure hydrated salt, but very unstable, losing both water and nitrous

oxide, and consequently becoming contaminated again with sodium hydroxide; if, however, it is promptly dried in a vacuum desiccator, it becomes anhydrous before it has undergone much decomposition, and is then quite stable in dry air. The amount of the hydrated sodium hyponitrite should be quite one-sixth of the calculated quantity, and the mother liquor will then be too poor in hyponitrite to be used as a source of silver hyponitrite.

A modification of the method, which gives an equally good yield, is to precipitate the salt by absolute alcohol instead of evaporating; the only precaution necessary is to prevent, as far as possible, the salt from becoming attached to the walls of the vessel. A large quantity of alcohol is required, because of the very large proportion of sodium hydroxide which is present. A few drops of the solution are added to the alcohol in a flask and at once violently shaken with it until the hyponitrite has completely solidified; then gradually the rest of the solution is poured in with very active agitation. If abundance of alcohol is used from the first, with thorough mixing, very little of the salt will remain in solution and very little adhere to the flask; with less alcohol at first, a notable quantity of the salt is lost by being kept in solution, for although it is afterwards slowly deposited, it is not then in a serviceable condition, and much salt is liable to adhere to the flask, which can, indeed, be dissolved out in water, and be reprecipitated by alcohol, but only with very great loss.

The action of sodium chloride on silver hyponitrite (see p. 106) is complex and quite unsuitable for the preparation of a solution of pure sodium hyponitrite. Nevertheless, such a solution, charged as it is with sodium chloride, and containing, besides, some silver hyponitrite dissolved in it, deposits sodium hyponitrite when mixed with much absolute alcohol, and this constitutes Jackson's second method of getting the salt; it always, however, contains a little chloride mixed with it.

The granular form of sodium hyponitrite is most marked in it when it has been separated from a highly concentrated solution of sodium hydroxide; when it is redissolved in a very little water and the solution rapidly evaporated in an exhausted desiccator, the salt separates as an almost structureless membrane on the surface, and there readily becomes opaque and apparently anhydrous. In the ordinary desiccator, a finely granulated crust forms. I have never obtained it in crystals. The salt, when quite freshly prepared, has an exceedingly mild, alkaline taste.

The attempts to determine the degree of hydration of the salt have been unsatisfactory because of its instability, but they point to the formula (NaON)₂+5H₂O. That formula requires 23.47 per cent. sodium, whilst analysis of the salt weighed as soon as it was almost

free from alcohol, gave 23.66 per cent. In place of 30.61 per cent for the hyponitrite ion, 28.10 per cent. was obtained by dissolving the salt in water and precipitating with silver nitrate, a deficiency fairly attributable to decomposition before the silver nitrite could be added; for, as proved by Zorn, this way of estimating hyponitrous acid is accurate. Loss of weight in the vacuum desiccator gave 44.91 per cent., whilst the calculated quantity of water is 45.92 per cent., but the difference is easily accounted for as due to loss of nitrous oxide, and, indeed, would be even greater but for the fact that this loss involves fixation of water by sodium oxide.

The anhydrous salt, somewhat decomposed, is non-coherent and opaque, and in appearance much like that of magnesia alba; heat is evolved when it dissolves in water, and it is insoluble in alcohol. The anhydrous salt only slowly takes up water from a solution of sodium hyponitrite. Heated in a closely-covered vessel, it yields nitrogen and sodium oxide mixed with some nitrate, $3(\text{NaON})_2 = 2\text{N}_2 + 2\text{Na}_2\text{O} + 2\text{NaNO}_2$. The salt bears a heat of 300° without decomposing, and then melts and effervesces; glass, platinum, and even silver are freely attacked by the fused mass, and the product hisses when water is added to it. Sodium hydroxide and nitrite are the solid products when the hydrated salt is quickly heated, and nitrous oxide, as well as nitrogen, is given off. Strong sulphuric acid decomposes the salt, with production of odourless, white vapours, and does not form nitrosylsulphate if the sodium salt is pure.

The salt, or a fairly concentrated solution of it, effervesces with a dilute acid like a carbonate. The solution, with the respective reagents, gives a precipitate of calcium hyponitrite and of most other hyponitrites at once. It dissolves a little silver hyponitrite and decomposes silver chloride (see the account of silver hyponitrite, p. 106). Dry sodium hyponitrite is not decomposed by carbon dioxide, and, since the hydrated or dissolved salt partly decomposes by interaction with the water, its power of fixing carbon dioxide does not indicate that it is directly decomposable by that substance. The solution, when boiled, decomposes moderately fast into hydroxide and nitrous oxide. If allowed to stand for a day, a trace of nitrite is formed (see p. 114).

Potassium Hyponitrite; Potassium Amalgam.

The preparation of a solution of potassium hyponitrite is throughout like that of a solution of the sodium salt. It is only necessary, therefore, to say something concerning the potassium amalgam which is required, concerning which as a reagent little or nothing has been published.

Merely for convenience in working, the composition of the potassium amalgam should correspond pretty closely, in parts by weight, to that recommended for the sodium amalgam, namely, (Hg14K), or 2800 of mercury to 39 of potassium, this being the weakest amalgam that is solid, a pasty amalgam like that of sodium not being obtainable. Although it crystallises in simple cubes, often very large, which are so sharp angled that they can hardly be introduced into a flask without fracturing it, these crystals are very easily crushed in a porcelain mortar, and are then in a state quite convenient for use. Sodium or potassium amalgam not stronger than here recommended (1 kilo. of mercury to 14 grams of alkali metal) is particularly easy to prepare in Draper's way, that is, by melting the sodium or potassium under solid paraffin and adding the mercury to it, at first very gradually. The operation can be performed on the open table. In spite of the fact that more heat is evolved, according to Berthelot's numbers, the action is less violent in preparing potassium amalgam than it is in the case of sodium amalgam. Potassium, also, nearly always requires to be well stirred with a glass rod to bring about its first contact with the mercury under the paraffin; sodium never does. When all the mercury has been added, either amalgam requires good stirring in order to dissolve all lumps, and should again be stirred when solidifying, in order to disturb crystallisation as much as possible. The specific gravity of the paraffin is about the same as that of potassium, but paraffin expands so very greatly in melting that the potassium readily sinks in it when it is in the liquid state. Muhlhaeuser, many years ago, melted sodium under petroleum and then added the mercury to it, and, in recent years, Nef has recommended the use of toluene, which boils freely by the heat produced in the union of the metals. But toluene could hardly be used in making potassium amalgam, because of its specific gravity.

A highly concentrated solution of potassium hyponitrite and hydroxide having been prepared, the hyponitrite can be precipitated by absolute alcohol, but only very incompletely, and some of what is precipitated is afterwards dissolved away in washing it with more alcohol. The preparation of this salt is, therefore, less satisfactory than that of the sodium salt.

Another way of making potassium hyponitrite is to decompose silver hyponitrite with exactly the right quantity of solution of potassium iodide. By rapid evaporation under reduced pressure, the solution can be concentrated, although with partial decomposition, preparatory to treating it with absolute alcohol, and it can even be dried up, so as to

^{*} This is probably due to the fact that the potassium presses but lightly upon the mercury on account of its specific gravity not greatly exceeding that of the paraffin, and not because of any chemical difference.

yield the impure solid salt. The cold of evaporation in a vacuum has sometimes caused the separation from the concentrated solution of hydrated crystals, which, however, melt when placed on filter paper; otherwise, the salt is obtained anhydrous in minute, prismatic crystals. The salt decomposes more rapidly than the sodium salt, but is stable when quite dry. It is soluble in 90 per cent. spirit, and slightly even in absolute alcohol. Its aqueous or alcoholic solution yields silver hyponitrite with silver nitrate, dissolves silver hyponitrite to some extent, and in other respects behaves like one of sodium hyponitrite. It has not been obtained sufficiently undecomposed to be fit for quantitative analysis.

Preparation of Silver Hyponitrite.

The hyponitrites were discovered through the production of the silver salt, and since that discovery this hyponitrite has been prepared and redescribed by many chemists; all deviations from the account I first gave of it are, however, incorrect, and the only additional observations that have been made are that it can be obtained in a purer state than I got it at first, and that it gives off nitric peroxide when heated. The very poor success in obtaining it in satisfactory quantity in recent years is remarkable (see p. 97); this seems to be due to erroneous methods of procedure, either in reducing the nitrite or in converting the sodium hyponitrite into the silver salt.

The concentrated solution of sodium hyponitrite and hydroxide, already described, is diluted and mixed with just sufficient silver sulphate or silver nitrate, dissolved in much water, to precipitate the hyponitrite; for it is unnecessary to neutralise the sodium hydroxide. (Neutralisation can, indeed, precede precipitation, if desired, as in preparing mercury and other hyponitrites, but in the case of the silver salt it is quite unnecessary, and there is a risk of loss of hyponitrite.) Silver sulphate should be used if it is essential to exclude nitrate from the silver hyponitrite; for, as will be shown, washing and reprecipitating are but imperfect means of purifying the precipitate. Supposing a half grammolecule of sodium nitrite to have been reduced, the alkaline solution, diluted to three times its volume or more, is mixed with 13 grams of silver sulphate or 14 grams of silver nitrate dissolved in about 3 litres of water, and the mixture stirred vigorously at once and continuously for 5 minutes, in order to convert the silver oxide into silver hyponitrite. After the precipitate has nearly all subsided, the turbid liquor, if bright yellow rather than brownish, is decanted and more silver solution added to it until, after stirring well, some brown silver oxide remains, when the whole is poured back and stirred up with the main precipitate, and then left to settle. Good daylight is almost essential

for judging the colour of the precipitate when finishing, but the precipitate should not be exposed to light more than is absolutely necessary.

After washing somewhat by decantation, the precipitate is stirred up with successive portions of highly dilute sulphuric acid (3 or 4 per mille) until this fails to become fully neutralised, and shows, therefore, when poured off and mixed with a drop of sodium carbonate, a slight yellow opalescence due to silver hyponitrite. The precipitate. after being washed with water by decantation until the washings no longer contain sulphate, is stirred up with water containing a trace of sodium carbonate, and, finally, again washed with water. It is then collected on a filter and dried in the dark in a vacuum. When thus dried, it may be heated for a time to 100° in dry air without change and become still drier. It is now usually as pure as it is possible to As, however, the operations are not always so perfectly carried out as to ensure this degree of purity, it is desirable sometimes to submit the salt to further treatment, preferably before it has been dried. In that case, it is dissolved, in portions at a time. in 3 per mille ice cold dilute sulphuric acid, and is either expeditiously filtered, if necessary, into some sodium carbonate solution. or, if not, is at once made alkaline with sodium carbonate. The reprecipitated salt is then treated with sulphuric acid and washed in exactly the same manner as the original precipitate. Even after reprecipitation, the silver hyponitrite obtained from 34.5 grams of sodium nitrite will weigh about 11 grams.

The process for preparing silver hyponitrite just given differs from that contained in my first paper in not neutralising the sodium hydroxide with acetic acid, in taking silver sulphate instead of nitrate, sulphuric acid in place of nitric acid, and sodium carbonate in place of ammonia, and in some minor details. The use of sulphuric acid is not new, that acid having been first used by van der Plaats, but the motive for the change is new and has been already given. Cold dilute sulphuric acid is not in the least less active than nitric acid in decomposing silver hyponitrite; in fact, unless very dilute, it is more active in consequence of silver sulphate crystallising out. Sodium carbonate (used by Haga and me in 1884, Trans., 45, 78) is to be preferred to ammonia for precipitating the salt, as being more sensitive, and because the last trace of ammonia is difficult to wash out of the silver salt (as Hantzsch and Kaufmann found, see p. 114). It is easy to ensure absence of all silver carbonate. along with complete precipitation of the hyponitrite, because of the solubility of the carbonate in the excess of carbon dioxide always present in the solution.

Properties of Silver Hyponitrite.

Silver hyponitrite is bright yellow, and when pale in colour it generally contains a trace of ammonia or loosely combined silver oxide. If along with such impurity there is also black silver suboxide, the colour becomes dull greyish-yellow, but when other impurities are absent, the presence of a little black oxide renders it somewhat bright green, as seen principally in the crude salt prepared by the hydroxyamidosulphonate method. The difference in colour observed has even suggested the possibility of the existence of different modifications, but there is really nothing to support this notion.

If precipitated from strongly alkaline solution, or from concentrated solutions of the sodium salt and silver nitrate, or in rubbing the calcium salt with strong solution of silver nitrate, silver hyponitrite is dense, but when precipitated by neutralising its solution in dilute acid, it is flocculent and bulky. When deposited from its ammoniacal solution through evaporation or large dilution with water, it is crystalline (Kirschner; but also see Paal and Kretschmer).

It is slightly more soluble in water than silver chloride, and is dissolved by very dilute nitric or sulphuric acid, so as to be recoverable on quickly neutralising the acid. The nitric acid required to dissolve it is considerable, being about 3 equivalents. The sulphuric acid solution very soon deposits silver sulphate. Acetic acid dissolves it only very slightly in the cold; phosphoric acid dissolves it, but not very freely. It is dissolved by ammonia solution, but only sparingly when this is very dilute, and the same salt can be recovered either by neutralising or dissipating the ammonia. It is also soluble in ammonium carbonate solution, and very slightly in ammonium nitrate solution. Of particular interest is its solubility to a slight extent in hyponitrous acid solution, and to a greater degree in solution of an alkali hyponitrite.

It is readily oxidised by strong nitric acid. Strong sulphuric acid acts energetically, the heat of reaction being itself quite sufficient to decompose some of the salt, a fact which accounts for the production of some nitric peroxide and nitrosyl sulphate (see effects of heating, p. 108). It is not decomposed by a cold solution of sodium carbonate, or by one of sodium hydroxide if it is weak. It is fully decomposed by its equivalent of potassium iodide in solution, but only imperfectly by a solution of sodium chloride, if the latter is not in considerable excess. When a solution of sodium chloride is shaken with excess of undried silver hyponitrite, decomposition ceases when the two sodium salts in the solution are in the proportion of 18 eq. of chloride to 25 eq. of hyponitrite, or, by weight, 4 of chloride to 5 of anhydrous

hyponitrite. Absolute alcohol in large excess effects a partial separation of the two sodium salts, as already described.

Silver hyponitrite in the moist state is not entirely stable, for it decomposes even at the ordinary temperature, although exceedingly slowly; light and heat quicken the change, the former modifying it to some extent. The decomposition is made evident by the salt losing its bright colour, by its answering to the iodide and starch test for a nitrite, and by its yielding up to water more silver salt (not nitrite, but nitrate apparently) than its own very slight solubility would account for. The salt may be washed with boiling water, or even be boiled with water, without any very apparent result, but continuous boiling not only has marked effect in decomposing it, but an action which grows in intensity, even though the water is frequently replaced. The water is found to contain silver nitrate, whilst the solid salt gives the reaction for nitrite. Masses of moist precipitate retain their colour outside while drying in a thermostat, but become greyish inside. Silver hyponitrite dissolved in a solution of sodium or potassium hyponitrite decomposes on standing, and very quickly on boiling, reduced silver being deposited and sodium nitrate formed in solution.

Bright diffused light causes enough change in a few hours-bright sunlight in a few minutes—to allow of nitrite being detected. colour change caused by light has been variously described; as a matter of fact, in the sufficiently pure salt under water, it is such that the bright yellow hyponitrite becomes covered with a somewhat bright brown, flocculent substance, very like silver oxide, which, perhaps, it is; the blackening or greying, which has been observed by others to be caused by light, must have been due to impurities, although time, as just described, brings about a greying of the salt. Silver hyponitrite is least sensitive to light when dry and exposed to dry air. The main change which occurs in the moist salt, slight as it is, is evidently similar to that caused by heat. The salt prepared by the hydroxyamidosulphonate method generally shows an unreal stability, due apparently to presence in it of a trace of sulphite, as will be explained when the properties of a hyponitrous acid solution are treated of; for, in that connection, it has to be taken into consideration that, like many other precipitated substances, silver hyponitrite is difficult to obtain of high purity. The very slight atmospheric oxidation of moist silver hyponitrite, described by Haga and me (Trans., 1884, 45, p. 78) I now regard as being, not the oxidation of the salt itself, but of nitric oxide produced by the very slowly decomposing salt, which is then retained as nitrate and nitrite in the salt: the result would be the same as if the salt itself were oxidised,

Effects of Heating Silver Hyponitrite.

In my first paper, it is stated that silver hyponitrite is decomposed by a moderate heat into nitric oxide, metallic silver, and a little silver nitrate—in this respect resembling silver nitrite, and that it does not fuse or exhibit any other change except that from a bright yellow to a silver-white colour. That is still a correct statement, so far as it goes, but it is imperfect. In 1887, van der Plaats stated that silver hyponitrite decomposes explosively when heated; presumably his preparation contained acetate. Thum, who, in 1893, rightly denied its explosive character, observed that, in decomposing by heat, the bright vellow salt becomes dark brown before assuming the white colour of silver, while Kirschner found (1898) that the salt became temporarily black. Thum's observation was due, I think, to the very dense red, almost opaque, hot nitric peroxide which then pours forth, and through which at times the solid mass does look very dark. Kirschner's observation may be due also to this cause, or to his hyponitrite having contained sulphite. However this may be, the salt decomposes with only the change of colour I have described, and in a lump of the precipitate the change can be followed by the change in position of the sharp boundary line between the bright yellow salt and the bright white metal, just as it can be followed in calcium oxalate decomposing by heat; there is no brown or black intermediate stage. Thum seems to have found no silver nitrate, but observed the production of dense red fumes even when the salt was heated in an atmosphere of carbon dioxide, and at a temperature not much (1) above 100°. From the important observation of the generation of nitric peroxide, he concluded that the decomposition of silver hyponitrite by heat is probably into silver, nitrogen, and nitric peroxide. I had, of course, seen, in my early work, the production of red fumes. but had attributed this to the nitric oxide meeting the air, and to the decomposition at a higher temperature of the silver nitrate which had been formed. The further study of the decomposition which I have made has proved that metallic silver, silver nitrate, nitric peroxide, nitric oxide, nitrogen, and possibly a trace of nitrite are always produced.

Having assured myself that nitric peroxide, as well as nitric oxide, is evolved by silver hyponitrite when heated, I exposed some to heat in a rapid current of carbon dioxide, in order to sweep away as fast as I could the nitric peroxide that was produced; for the production of nitric peroxide may sufficiently account for that of silver nitrate secondarily. The nitric peroxide and the metallic silver could give the nitrate (Divers and Shimidzu, Trans., 1885, 47, 630), but it seems improbable that these two substances being produced would then

immediately interact at the same temperature. There is, however, no reason why the nitric peroxide of the decomposed part of the salt should not act on the undecomposed portion and thus produce nitrate, such interaction readily taking place. My experiment recorded above was instituted to see whether I could not almost prevent the formation of nitrate. The attempt failed, for I found silver nitrate in the residue equivalent to as much as $\frac{1}{17}$ th of the total silver, but this result does not disprove that the nitrate really is formed in the way suggested.

The nature and composition of the gaseous products were ascertained by heating the salt in a vacuum. The quantity of salt taken was in each experiment so proportioned to the capacity of the little flask or bulb in which it was heated that the volume of the gases at the common temperature and pressure should be a little less than the capacity of the bulb. The air was removed from the bulb holding the salt by means of the mercury pump, while the bulb was kept in boiling water to ensure the dryness of the salt. When exhausted, the bulb was sealed off, and the silver hyponitrite decomposed by heating the bulb in a bath. Thus heated in the absence of air and moisture, the salt exhibits scarcely any change below 140°, and only slow decomposition between 140° and 160°, but above these temperatures the change is soon complete. The metallic silver is slightly caked together, presumably by the silver nitrate, and the gases are faintly red between 140° and 150°, and orange-red at 160° and above. On allowing the vessel to cool, the gases become colourless, but regain their colour just as before when the vessel is again heated, and these changes can be repeated any number of times.

To examine the contents of the bulb when cold, its point was broken off under water, and the small rise of water into the neck of the bulb marked; then the bulb was transferred to a small trough of strong solution of sodium sulphite in order to absorb the nitric oxide (this vol., p. 82). After an hour or longer, the residual gas was examined and measured by bringing the bulb mouth upwards, testing the gas as to odour and power to support combustion, and then filling it with water from a burette up to the mark already made, and afterwards to the mouth in order to learn the volumes of the gases when corrected for temperature and pressure. The volumes could be only approximately measured in this way, but quite well enough for the purpose. The metallic silver was weighed, and from its weight and that of the hyponitrite, that of the silver nitrate became known. In one experiment, the bulb was at once freely opened to the air, and the gases rapidly blown out; in this way, the nitric oxide showed its presence by reddening in the air, and both the silver and the silver nitrate were directly determined.

These experiments established the production of nitrogen, as well as that of the other substances, and the non-production of any appreciable quantity of nitrous oxide. The quantitative results were that, when the decomposition is slowly effected, as between 140° and 160°, silver hyponitrite yields about 27 per cent. of its nitrogen in the free state, and about 20 per cent. when the decomposition is rapidly accomplished at higher temperatures. The silver nitrate was formed in quantities corresponding with those of the nitrogen, according to the equation $3(AgON)_{o} = 4Ag + 2AgNO_{o} + 2N_{o}$, but that, of course, proved nothing, since the whole of the nitrate might have been formed by the nitric peroxide during the cooling, as certainly much of it must have been. On the other hand, the limited quantities of nitrogen generated gives full proof that much nitric oxide is either primarily formed or comes from interaction between hyponitrite and peroxide, besides what undoubtedly comes from the interaction of the nitric peroxide and metallic silver during the cooling. Were none of the nitrogen of the salt to become nitric oxide, the free nitrogen would be half of the total nitrogen, instead of only three- or fourfifteenths as found.

From the facts observed, it seems to me to be highly probable that silver hyponitrite decomposes into silver, nitrogen, and nitric peroxide, according to the equation $2(AgON)_2 = 4Ag + N_2 + 2NO_2$, and that interaction then occurs between the hyponitrite not yet decomposed and some of the nitric peroxide, thus: $(AgON)_2 + 4NO_2 = 2AgNO_3 + 4NO$, and, therefore, that the decomposition of silver hyponitrite into silver and nitric oxide does not occur directly.

It remains to explain the absorption and regeneration of nitric peroxide by cooling and heating the gases in contact with the solid residue of the decomposed hyponitrite. The interaction of silver and nitric peroxide in the cold, already referred to, explains the disappearance of the nitric peroxide, half of its nitrogen becoming nitrate and half nitric oxide. The regeneration of nitric peroxide at such low temperatures as those in the neighbourhood of 150° is explained by experiments of mine recorded in a separate note (this vol., p. 83). The silver nitrate and nitric oxide interact to produce nitric peroxide, and at first nitrite, but ultimately silver itself, $AgNO_8 + NO = Ag + 2NO_2$.

As to the Existence of Silver Nitrito-hyponitrite, Nitrato-hyponitrite, and Nitrato-nitrite.

Silver Nitrato-nitrits.—I have made new experiments on the union of silver nitrate with silver nitrite, first examined by me in 1871 (Trans., 24, 85). Silver nitrite, mixed with a little less than its equivalent of silver nitrate, suffers only slight decomposition until it

melts along with the nitrate at about 130°. The fused salts solidify at about 125° to a translucent, greenish-yellow, crystalline mass, except in the uppermost part, where it is opaque from the presence of bubbles and metallic silver. This upper part removed, the rest can be fused again without suffering further change, and even be heated nearly to 180° without decomposing. Silver nitrite, heated alone, shows marked change of colour when the temperature has reached 120°, gives red fumes at about 140°, and very freely decomposes below 180° without showing signs of fusing. Silver nitrate does not fuse below 217° (Carnelly). The low melting point of the mixture of the two salts, and the increased stability of the nitrite, are, however, the only facts showing that there is any chemical union, for water separates the two salts.

Non-existence of Nitrato-hyponitrite.—Silver hyponitrite (4 parts) and silver nitrate (5 parts), in intimate mixture, were heated in a bath. No change was observed until 175° was reached, when fusion and the evolution of red fumes occurred. The hyponitrite had then disappeared, and the fusion may be attributed to the decomposition of the hyponitrite, as usual, into nitric oxide, among other things, and to the interaction of this nitric oxide with some of the nitrate to form the fusible nitrato-nitrite.

The attempt was also made to prepare a compound of the two salts in presence of water, there being some grounds to expect success. Calcium hyponitrite, a nearly insoluble salt, was ground up with excess of a very concentrated solution of silver nitrate, and a dense and strongly yellow precipitate obtained, which was washed with water until all the calcium salt had been removed; the precipitate was still yielding up a little silver nitrate when the washing was stopped. Drained on a tile and dried in a vacuum, it proved to be somewhat sensitive to light and to heat, but, as it contained 76.94 per cent. of silver, and could have been washed more free from silver nitrate, a combination of the two salts stable in water does not exist. All that can be said is that silver hyponitrite requires long washing to remove the last portions of silver nitrate.

Nitrito-hyponitrite also non-existent.—In a paper already referred to, I have recorded obtaining a minute quantity of what appeared to be hyponitrite, when partially decomposing silver nitrite by heat, that is, a bright yellow substance insoluble in water and soluble in ammonia. I have failed to get this again. Silver hyponitrite and silver nitrite, heated together, show no change until decomposition and the escape of red fumes occur, and then all hyponitrite has been destroyed.

When making known his observation of the interaction of hydroxylamine and nitrous acid in 1893, Paal stated that, from a solution of

alkali hyponitrite which also contained nitrite, silver nitrate had precipitated a substance which, although it was like silver hyponitrite, proved to be a silver nitrito-hyponitrite. It gave no silver nitrite, even to hot water, and could be dissolved in cold dilute nitric acid, and be reprecipitated with ammonia without suffering change in composition. It was less stable than the simple hyponitrite when heated, gave the reactions of a nitrite along with those of a hyponitrite, and yielded numbers (not quoted), on analysis for silver, which agreed nearly with that required by the formula Ag. N.O.. Ten years previously, Berthelot and Ogier, probably under similar conditions, got similar results, except that they were led by their analysis to give the formula Ag.N.O. to the substance they had obtained. It is true that, in spite of endeavours to purify it, silver hyponitrite retains with obstinacy enough nitrite to give the iodide and starch reaction for a nitrite, and that it often, through the presence of impurities, gives low results for the silver; but, beyond these admissions, I cannot subscribe to the accounts given by the chemists just named as to the existence of compounds of silver hyponitrite with silver nitrite.

I have reduced sodium nitrite by sodium amalgam as usual, and dissolved in the solution one-sixth as much more sodium nitrite as had been reduced, thus getting hyponitrite and nitrite together in solution in about equivalent proportions, in accordance with the experience recorded in this paper. The precipitation of silver hyponitrite was then proceeded with, in one experiment, without previous neutralisation of sodium hydroxide, and in another experiment after neutralisation of the alkali. The result was the same in both experiments. There was a bright yellow precipitate, not noticeably different from ordinary hyponitrite, and the mother liquor retained much alkali nitrite or silver nitrite in the respective cases; the precipitate was repeatedly washed with cold water, but the washing was stopped when very little silver was being extracted. It proved to be somewhat sensitive to light and heat. It was dried in the cold and in a vacuum. and the silver was then determined; this was 76.9 per cent. Nitrite could be easily detected in it, but the compound Ag, NoO, would have only 74 per cent. of silver, and Ag, N, O, only 76 per cent. this, by prolonged washing the hyponitrite can be made much purer. These experiments, therefore, afford no evidence of the existence of such a compound as Paal has described.

Properties of a Solution of Hyponitrous Acid.

Solutions of hyponitrous acid are always prepared in one way, namely, by decomposing silver hyponitrite with just sufficient dilute hydrochloric acid. Hyponitrous acid has been obtained by Hantzsch

and Kaufmann in crystals very deliquescent and very unstable, by using dry ether in place of water in its preparation. The acid in dilute solution reddens litmus not so strongly as nitric acid, but much more than carbonic acid. On drying the reddened litmus paper, it becomes blue again. A solution of the acid becomes neutral to litmus when half the quantity of baryta water or alkali required to form the normal salt has been added (Zorn), and such a solution, by decomposition, soon acquires the property of blueing red litmus paper. When neutral to litmus, the solution is also neutral to phenolphthalein (Thum). When neutralised with baryta, and very rapidly evaporated under reduced pressure, hyponitrous acid yields an acid salt which is crystalline and extremely unstable (Zorn).

It decomposes silver carbonate, if not also lead and other carbonates; it also decomposes silver nitrate and sulphate. It does not oxidise hydrogen iodide (iodide and starch reagent), and is not oxidised by iodine solution or by the air. It is oxidised by nitrous acid and the stronger oxidising agents. No way of deoxidising or hydrogenising hyponitrous acid is known; it entirely resists the action of sodium amalgam, and also, according to Thum, that of zinc and sulphuric acid. Ethylic hyponitrite is reduced, apparently, by tin and acetic or hydrochloric acid to alcohol and nitrogen, according to Zorn, but as, also according to him, it slowly decomposes by itself, when moist, into nitrogen, alcohol, and aldehyde, there is sufficient reason to doubt that this reduction by tin and acid is anything more than the hydrogenisation of the aldehyde.

Hyponitrous acid slowly decomposes into nitrous oxide and water. A strong solution soon effervesces, gently in the cold, freely when heated, just like a solution of carbon dioxide, and some hyponitrites in presence of only a little water effervesce with an acid. A solution of one or two grams of the acid in a litre of water kept in ice hardly falls noticeably in strength in one hour, but at 25—30° it may lose a sixth of the acid by decomposition in 24 hours; at a lower temperature, Thum observed a loss only half as great in the same time. Alkali hyponitrites in solution also decompose into nitrous oxide and alkali, gradually in the cold and rapidly when heated; alkali hydroxides impede the decomposition, and when highly concentrated stop it altogether, apparently (see p. 98); neutralisation of the alkali even by carbonic acid hastens the decomposition, as a matter of course, but there is no evidence that carbonic acid is able to decompose a hyponitrite, as it has been said to do.

Hyponitrous acid solution dissolves silver hyponitrite slightly. The alkali salts of hyponitrous acid dissolve silver hyponitrite somewhat more freely, and also decompose silver chloride (see p. 102);

they give precipitates with barium and calcium salts, and with solutions of most metallic salts.

Other substances are liable to be present in the solution of hyponitrous acid, and this fact has certainly caused the properties of the acid to be wrongly described in some respects. In one point, this is the case in my first paper, in which, however, there was a warning that the crude solution of the acid, which had been examined, might have reacted as it did partly through the presence of other unrecognised substances in it. That solution decolorised iodine water, and prevented the action of nitrous acid on an iodide; this, however, was not due to the hyponitrous acid, but to a very little hydroxylamine, the presence of which was unrecognised. Kirschner has again given to hyponitrous acid the property of decolorising iodine water to a slight extent. In his case, the substance acting on the iodine must have been a trace of sulphur dioxide, for he made his solution of the acid from silver hyponitrite that had been prepared by the hydroxyamidosulphonate method. I can confirm the accuracy of his observation. Even when the silver hyponitrite has been most carefully precipitated so as to avoid all sensible precipitation of sulphite, and has been dissolved in dilute acid and reprecipitated, it still gives a solution of hyponitrous acid capable of acting on a very little iodine water; but then no more iodine was taken up although there was hyponitrous acid in the solution. On the other hand, the acid prepared from silver hyponitrite not derived from hydroxyamidosulphonate does not decolorise iodine at all, as Thum first pointed out.

Hyponitrous acid, according to van der Plaats, liberates iodine from potassium iodide; according to Thum and my first paper, it does not, whilst according to Hantzsch and Kaufmann it is only just at first that it does not do so. The last-named chemists, therefore, state that the acid does not itself liberate iodine, but quickly begins to yield nitrous acid which does liberate it. They also found hyponitrous acid to yield ammonia, but in a later publication Hantzsch and Sauer state that the ammonia was an impurity in the silver hyponitrite from which the acid had been prepared. Even with the simultaneous formation of the ammonia, it is difficult to understand the generation of nitrous acid. These authors, invoking the aid of tautomerism, suppose that the hydrogen leaves oxygen for nitrogen, giving the unknown substance HN:O, which then becomes NH, + N₂O₂, and these again pass into HNO₂ + N₂ + OH₂. In place of this series of improbable—I would say, unnatural—changes, I suggest that, if indeed such change occurs at all, it must be into water, nitric oxide, and nitrogen, the nitric oxide then oxidising to nitrous acid. But I am strongly disposed to deny that hyponitrous acid decomposes of itself into anything but what are certainly its main products, nitrous oxide and water. My reasons are several. First, there is the unlikelihood that the diazo-radicle, N:N, should resolve itself into mono-nitrogen compounds, such as NO, NH, NOOH or (NO), O, instead of (N.)O. Secondly, there is the fact that time comes in as the condition of the production of nitrous acid, and that a rise in temperature does not. A solution of hyponitrous acid of fair purity, if boiled or quickly evaporated gives nothing but nitrous oxide and water; and only very slowly and to a very small extent does nitrous acid appear in a cold solution of the purest acid. Thirdly, the greater the care taken to reduce and exclude all nitrite in preparing the hyponitrous acid solution, the longer will be the time before any sensible quantity of nitrous acid develops, and the more gradually will the quantity increase. From these facts, the almost necessary inference is that the whole of the nitrite has never been entirely removed or excluded in preparing the acid, and that what has been left, although too minute in quantity to affect the iodide test (which requires 1 in 20 millions, according to Warington), yet multiplies itself by interaction with the hyponitrous acid, forming nitric oxide, which is further oxidised to nitrous acid by the air dissolved in the solution (HNO), +2HNO, =2H,0+4NO-4HNO,. This aërial oxidation can be demonstrated in such a solution of hyponitrous acid as that which Hantzsch and Kaufmann employed in their experiments, which gave the blue of the iodide test almost immediately; it is only necessary to leave one portion of the solution in a deep, narrow vessel, such as a test tube half full, and another portion in a shallow basin for 10 minutes, and then apply the test, when the solution in the basin will be found to liberate more iodine than that in the tube. If, in reducing the sodium nitrite, its concentrated solution is shaken with excess of the amalgam for an hour or two after its main reduction, and the solution is then either diluted, acidified cautiously with dilute sulphuric acid, and tested, or is precipitated by silver sulphate, away from the light as far as practicable, and the precipitate washed in the dark and converted into the acid and tested, either solution, when mixed with the iodide reagent, will not blue in the least for an hour or more in the dark, and provided the constituents of the reagent are pure enough and properly used.*

Against the view, which may be advanced, that hyponitrous acid becomes nitrous acid through exidation by the air, I must point out

[•] My way of applying the test is that followed by Warington (*Chem. News*, 1885, 51, 39), except that, having potassium iodide of high quality, I used it instead of Trommsdorf's zinc iodide solution. In the dark, a blank test will remain for hours without the least blueing. There is no advantage in using acetic acid in place of pure sulphuric or hydrochloric acid.

that it is difficult to admit that if the nitrous acid has such origin, it should form so very slowly. A way occurred to me which must be used for deciding this point, so far as the exclusion of nitrous acid goes, but it has, in my opinion, not served to do so. If, in preparing sodium oximidosulphonate, the sulphur dioxide is used in excess, every trace of nitrite ought, presumably, to be sulphonated; if, then, the oximidosulphonate is fully hydrolysed into hydroxyamidosulphonate, as it presumably can be, then, when the latter is converted into hyponitrite and sulphite by potassium hydroxide, there will be no oximidosulphonate present to simultaneously revert to nitrite and sulphite. Therefore, the silver hyponitrite from such a source should be obtainable absolutely free from nitrite, and should furnish a solution of hyponitrous acid also free from nitrous acid. Such silver hyponitrite I endeavoured to prepare, and then tested the acid got from it. The issue was, however, complicated by the fact that such an acid is not quite free from sulphurous acid, as was shown by its decolorising a minute quantity of iodine solution. That it also did not act for a time on the iodide and starch reagent was due in part to this cause. solution did, however, give a blue coloration with the reagent sooner than a corresponding blank test. But this was no proof that hyponitrous acid passes spontaneously into nitrous acid, for, first, there is the possibility of nitrous acid having been present through incomplete sulphonation and hydrolysis in preparing the hyponitrite; this nitrous acid would, indeed, have been converted into nitric oxide by the sulphurous acid retained by the silver salt, but when all this was gone, the nitric oxide would have become nitrous acid again by Secondly, it is almost certain that the oxidation of the sulphurous acid by the air would have induced oxidation of some hyponitrous acid, in accordance with the observations of Mohr, M. Traube, van't Hoff and Jorissen, Engler and Wild, Bach, &c.

Quantitative Estimation of Hyponitrous Acid.—Hyponitrous acid can be estimated accurately, both gravimetrically (Zorn) and volumetrically (Thum). Solutions of the free acid, or of its alkali salts in water, or of its other salts in very dilute and cold nitric acid are mixed with excess of silver nitrate, and then the free acid is just neutralised with sodium carbonate or with ammonia. The washed precipitate is either dried and weighed as such, or weighed as metal or as chloride.

Volumetrically, the acid can be estimated in solution in the free state and unmixed with any other acid, by adding excess of solution of potassium permanganate, leaving it for a quarter of an hour, then adding sulphuric acid, allowing it to remain for another quarter of an hour, warming to 30°, adding a known quantity of oxalic acid sufficient to decolorise, and, finally, titrating back with permanganate. The hyponitrous acid is thus oxidised to nitric acid. The oxalic acid should

be decinormal, and the solution of permanganate be volumetrically equivalent to it. Ferrous sulphate is unsuitable for use in place of oxalic acid. The process is an excellent one. Hantzsch and Sauer failed to get good results, because they deviated from Thum's directions by acidifying the permanganate before adding it to the hyponitrite. Kirschner also was unsuccessful with this process, but his failure is also explained by his deviation from Thum's directions. He added nearly insoluble salts, such as the barium, strontium, or silver hyponitrite, to the potassium permanganate, so that the base of the salt was present, and the hyponitrous acid locally in excess of the permanganate; he then added the sulphuric acid, apparently immediately, and used ferrous sulphate for titrating back.

Taking 5 c.c. of normal hydrochloric acid, largely diluting it, adding ice and a cream of precipitated silver hyponitrite so as to exactly use up all the hydrochloric acid, making up to 100 c.c., and decanting from the bulk of the silver chloride, I obtained a solution which, although somewhat turbid from silver chloride, gave, in successive portions of 20 c.c., all tested within an hour, quantitative results corresponding well with 0.155 gram hyponitrous acid in 100 c.c., that is, the quantity equivalent to the hydrochloric acid taken; next day, the remainder of the solution (in very hot weather) showed the presence of 0.131 gram of the acid in 100 c.c.

Thum found that, in alkaline solution, alkali hyponitrite is quantitatively converted into nitrite by permanganate. Although I have not examined this point myself, I find that nitrite is thus formed, and that nitric acid is formed in Thum's acid permanganate method. Kirschner doubts that either is produced.

Barium, Strontium, and Calcium Hyponitrites.

Barium hyponitrite has been obtained by Zorn, Maquenne, and Kirschner, and is most simply prepared by adding barium chloride to a concentrated solution of sodium hyponitrite and stirring well. It is crystalline, almost insoluble, and an unstable and exceedingly efflorescent salt, but Kirschner has succeeded in determining its water of crystallisation satisfactorily. Its formula is $BaN_2O_2 + 4H_2O$. A crystalline acid salt exists (Zorn).

Strontium hyponitrite, $SrN_2O_2 + 5H_2O$, Maquenne, Kirschner.

Calcium hyponitrite, CaN₂O₂ + 4H₂O, Maquenne, Kirschner. This is crystalline, very sparingly soluble, stable, not losing its water even over sulphuric acid. I find that it can be easily precipitated from a fairly concentrated solution of sodium hyponitrite, and can thus be prepared more easily than in the ways followed by Maquenne and by

Kirschner, using the silver salt. On account of its stability, it is a good hyponitrite to keep in stock. It is sufficiently soluble for its solution to serve to show the reactions of a hyponitrite with silver, mercuric, mercurous, copper, lead, and other salts.

Calcium, Strontium, and Barium Hyponitrosoacetates.

Some remarkable salts have been described by Maquenne, having the composition expressed by the formulæ

 $\frac{\text{CaN}_2\text{O}_2, \text{Ca}(\text{C}_2\text{H}_8\text{O}_2)_2, (\text{C}_2\text{H}_4\text{O}_2)_2 + 4\text{H}_2\text{O}; \text{SrN}_2\text{O}_2, \text{Sr}(\text{C}_2\text{H}_8\text{O}_2)_2, (\text{C}_2\text{H}_4\text{O}_2)_2 + 3\text{H}_2\text{C}}{\text{BaN}_2\text{O}_2, \text{Ba}(\text{C}_2\text{H}_8\text{O}_2)_2, (\text{C}_2\text{H}_4\text{O}_2)_2 + 3\text{H}_2\text{O}}.$

I have prepared and partly analysed the calcium salt, following Maquenne's process, which is to dissolve calcium hyponitrite in 30 per cent. acetic acid until the new salt begins to crystallise out. I kept the acid at about 50° while dissolving in it nearly as much of the calcium salt as it would take up, the salt being deposited on cooling. It is remarkable that this can be done without causing more than very slight effervescence. The salt crystallises in short prisms, stable for many days, very soluble in water, in which it gives, with silver nitrate, the yellow hyponitrite. In spite of its acid composition, it is neutral or even slightly alkaline to litmus. To account for its existence and neutral reaction, I suggest for it the constitution expressed by the formula

$$Ca(OAc)_{2}$$
, $Ca < \frac{O \cdot N_2 \cdot OAc}{OAc} + 5H_2O$.

This represents it as being normal calcium acetate with one-fourth of its oxylic oxygen replaced by the hyponitrite radicle, or as a double anhydride of calcium acetate and hyponitrite. It is thus made out that a constitution analogous to that of a (hypo)nitrososulphate, a determined by Haga and me (Trans., 1895, 67, 1098),

$$Ca < 0-N_2 > 0.$$

Simple hyponitrosoacetic acid, $C_2H_8O \cdot O \cdot N_2 \cdot OH$, would be isomer with acetonitrosohydroxamic acid, $C_2H_8O \cdot N(NO) \cdot OH$, which Hantzs and Sauer have been trying to prepare. The hyponitrosoacetat are much more stable in water than the (hypo)nitrososulphates, difference perhaps connected with the fact that sulphuric acid ionil largely, while both acetic acid and hyponitrous acid ionise very littleated with water, the hyponitrosoacetates decompose like the (hyponitrososulphates do in cold water.

Mercuric Hyponitrite.

Mercuric hyponitrite is a particularly interesting salt and has not as yet been described. Rây has, indeed, described some compounds which he regards as being basic mercuric hyponitrites, but obtained under conditions suggesting the probability that they are something quite different; moreover, he has not as yet proved them to be compounds of this class. One of them he obtained by the interaction of solutions of mercuric nitrite and potassium cyanide, a very interesting and remarkable result, should it be confirmed. In any case, his precipitates appear to have nothing at all in common with the normal salt here described, and cannot be obtained in the ordinary way. The existence of this salt was indicated by me in 1871.

Mercuric hyponitrite is obtained from sodium hyponitrite and mercuric nitrate by precipitation; the solution of sodium hyponitrite and hydroxide, obtained by reducing sodium nitrite, is largely diluted and, while ice cold, nearly or quite neutralised with dilute nitric acid; it is then (mercurous nitrate serving as indicator, see p. 97) poured into a mercuric nitrate solution, which must not be in excess and should contain as little free acid as possible. The slightly turbid mother liquor is quickly decanted from the precipitate formed, and after being neutralised with sodium carbonate is mixed with more mercuric nitrate, the whole poured back on to the main precipitate, stirred up with it, and soon again decanted. The precipitate should be washed quickly by decantation, since it is liable to be quickly destroyed by the slightly acid mother liquor.

It is a flocculent, cream-coloured precipitate, easily washed on the filter, and dries up to a light buff-coloured powder, this colour being due, probably, to incipient change into the mercurous salt. Dried quickly in the air, on a porous tile, it is hydrated, having the formula (HgN_cO_c)_c + 3H_cO, but if dried in the desiccator it is anhydrous. Being a little sensitive to light, it should be dried in the dark. dissolves in hydrochloric acid and in sodium chloride solution, but it is unstable, changing into the mercurous salt, and, therefore, is liable to show turbidity in the chloride solutions. The mercury, precipitated as sulphide from a solution of the anhydrous salt in hydrochloric acid, was found to be 76.71 per cent., the formula HgN,O, requiring 76.92 per cent. Its solubility in excess of sodium chloride does not prevent mercuric chloride giving a precipitate with sodium hyponitrite. The solubility of the salt in sodium chloride is a qualitative proof of its normal composition. The alkalinity of the solution is caused by the sodium hyponitrite generated in it. Potassium hydroxide at once decomposes mercuric hyponitrite into oxide, without showing any

tendency to produce basic salts. In very dilute alkali, the precipitate is slightly soluble.

What makes this salt so remarkable, not only as a hyponitrite, but as a mercuric salt, is the nature of the decomposition which it under-Slowly or quickly, it decomposes into mercurous hyponitrite and nitric oxide—some of the latter, oxidised by the air, converting some hyponitrite into nitrate. No other mercuric salt decomposes into mercurous salt, although many cupric salts change into cuprous Ferric oxalate shows just the same kind of change, namely, into ferrous oxalate and carbon dioxide. The most closely related change, however, is that of sodium (hypo)nitrososulphate into sulphite and nitric oxide, the very phenomena being similar, so that, except for the colour change. I might describe my experience with this salt in the words of the paper by Haga and me on sodium (hypo)nitrososulphate (Trans. 1895, 67, 1095). Thus, having on one occasion left some grams of salt all night in the desiccator in the form of a pressed cake, just as removed from the filter, I noticed, when weighing it between watch-glasses, that it was losing weight on the balance-pan. When the glasses were opened, a strong nitrous odour was observed, the cake soon became grey, white on the surface, and, being left loosely covered, grew very hot and gave out torrents of nitric oxide; it then cooled, and underwent no further change, even in the course of months. The whitish colour of the cake was found not to penetrate beyond a millimetre into it, the inside being of a uniform yolk-yellow, and consisting of mercurous hyponitrite. The surface-coating proved to be mercurous nitrate, largely soluble in water, and had evidently been produced with the assistance of the oxygen of the air. Not always, however, does the change occur in this striking and rapid way, its progress being gradual and almost imperceptible until complete.

Mercuric hyponitrite is decomposed by heat largely into mercuric oxide and nitrous oxide, but partly into metal and nitric oxide.

Other Hyponitrites.

Mercurous Hyponitrits.—This salt has been prepared and analysed by Thum (Inaug. Diss., Prag. 1893), who used sodium hyponitrite and mercurous nitrate in obtaining it. The possibility of getting it by the spontaneous decomposition of mercuric hyponitrite has just been described. Rây has also evidently obtained it in a very impure state, not further examined. It can be prepared in the same way as mercuric hyponitrite, using mercurous nitrate in place of mercuric nitrate. It is of a full yellow colour, is blackened by even the weakest solution of alkali, and is soluble in dilute nitric acid, from

which it can be precipitated by sodium carbonate. It is a stable salt, but is blackened by bright light. Its decomposition by heat resembles that of the mercuric salt, except that much more metal is produced, as is natural. Composition, (HgON)₂.

Cupric Hydroxide Hyponitrite.—This salt was described by me in 1871, and was also obtained by Kolotow in 1890, but was first fully examined by Thum, and has again been examined by Kirschner; being a basic salt, its precipitation from normal sodium hyponitrite leaves an acid mother liquor, on neutralising which much more of the salt precipitates. It is of a bright pea-green colour, and very stable. It may be boiled with water without losing its colour, but is decomposed by sodium hydroxide and is soluble in dilute acids and ammonia. Thum has shown its composition to be Cu(OH)NO. It gives water, cupric and cuprous oxides, and nitrous and nitric oxides when heated. By adding copper sulphate in excess to hydroxylamine sulphate and then a very little ammonia, it can also be precipitated in small quantity.

Cuprous hyponitrite cannot be formed. I have tried to get it by precipitating sodium hyponitrite by copper sulphate in presence of free hydroxylamine, but, first, cuprous oxide precipitated and then, by aërial oxidation, the basic cupric hyponitrite, which in composition is equivalent to that of cuprous hyponitrite combined with hydroxyl (see above).

Lead Hyponitrite.—This salt was also briefly described by me and has been prepared and analysed by Thum; Kirschner has again prepared and analysed it, but not in a pure state. The precipitate is cream-yellow and flocculent, but soon becomes very dense and sulphuryellow; its first state is probably that of a hydrate; Kirschner has mistaken it for a basic salt. The yellow salt is PbN₂O₂. As Thum has pointed out, the yellow precipitate, when formed in a weak acid solution, is crystalline and just like ammonium phosphomolybdate. It is soluble in dilute nitric acid, and is decomposed by sodium hydroxide, but not by sodium carbonate in the cold.

Ammonium Hydrogen Hyponitrite.—This salt has been described by Hantzsch and Kaufmann, who found it to be exceedingly unstable, as was to be expected. That the normal salt could not exist had already been pointed out by me, and by Zorn; D. H. Jackson believes, however, that he did obtain it in small quantity in prismatic crystals, but this is exceedingly improbable.

Rthylic Hyponitrite.—This alkylic salt was prepared by Zorn, and its vapour-density taken by him. It is very explosive, and is not saponified by potassium hydroxide. In the moist state, it slowly decomposes into nitrogen, alcohol, and aldehyde.

Benzylic Hyponitrits.—Hantzsch and Kaufmann have prepared

benzylic hyponitrite and determined its molecular magnitude cryoscopically. It undergoes similar decomposition to the ethylic salt.

Constitution of the Hyponitrites.

Molecular Magnitude.—In my first paper, nothing could be said as to the molecular magnitude and constitution of the hyponitrites. In 1878. Zorn fully determined their molecular magnitude, finding it to be that containing No, first, by establishing the existence of an acid barium salt and illustrating the similarity of hyponitrites to carbonates (a point which had already been noticed by me), and then by preparing ethylic hyponitrite and taking its vapour-density at reduced pressure (Hofmann's method). It would, therefore, be unjust to the memory of this chemist to admit Hantzsch's claim (Annalen, 1898, 299, 68) to have finally established this point by determining cryoscopically, in conjunction with Kaufmann, the molecular magnitude of hyponitrous acid in water and of benzylic hyponitrite in acetic acid, valuable as these determinations are. The possibility of determining the molecule of the acid in its solution in water rests upon the fact, also ascertained by these chemists, that the acid only slightly ionises even in very dilute solution. Maquenne, by a somewhat uncertain form of the cryoscopic method, has also shown that, in calcium hyponitrosoacetate, the hyponitrite radicle cannot be less than NoOo. strong alkalinity of the alkali salts, and the want of action on litmus of their partially-neutralised solution, first pointed out by me, and the solubility, although only slight, of silver hyponitrite in hyponitrous acid solution (Thum) and in alkali hyponitrite solution, are also facts in accordance with the dihydric composition of the acid. Other chemical evidence of the diazo-grouping in hyponitrites is afforded by the fact of the difficulty, if not impossibility, of deoxidising or hydrogenising them (see p. 113). The derivation of hyponitrites from the interaction of hydroxylamine and nitrous acid would only afford evidence of the diazo-magnitude of the molecule, if the hyponitrite produced were much larger in quantity than what can be obtained from hydroxylamine by other oxidising agents, or from nitrous acid by other reducing agents.

My colleague, Assistant Professor Ikeda, has kindly made some determinations of the molecular magnitude of sodium hyponitrite by Loewenherz's method (*Zeit. physikal. Chem*, 1896, 18, 70), in which the lowering of the freezing point of melted hydrated sodium sulphate by another sodium salt is observed; Loewenherz found that sodium salts behave towards the water of hydrated sodium sulphate almost as non-electrolytes. Prof. Ikeda, in his experiments, employed sodium thiosulphate in place of sulphate, but only because he had been working

with that salt, and had had large experience with it. Unfortunately, the anhydrous sodium hyponitrite I could furnish at the time was contaminated with 4 or 5 per cent. of carbonate (same mol. wt.), so that the determination of the molecular magnitude can only be regarded as approximate. But it is amply sufficient to decide between NaON = 53, and $(NaON)_2 = 106$, if that were any longer necessary, after Zorn's decisive researches, supplemented by those of Hantzsch and Kaufmann. Prof. Ikeda has given me the following details.

M. p. of Na₂S₂O₃ + 5H₂O = 48·4° (Tilden found 48·5°); H. of fusion = 42·8 Cal. (Ikeda); Wt. of thiosulphate used = 40·9 grams; Wt. of sodium hyponitrite used = g grams; Dp. of solidifying pt. = ΔT° ; Mol. wt. of hyponitrite = m.

$$m = \frac{1}{\Delta T} \cdot \frac{g}{40.9} \cdot \frac{2(273 + 48.4)^2}{42.8} = \frac{g}{\Delta T} 118.1.$$

$$g. \qquad \Delta T^{\circ}. \qquad m.$$

$$0.152 \qquad 0.115 \qquad 156$$

$$0.467 \qquad 0.509 \qquad 108$$

$$1.066 \qquad 1.260 \qquad 100$$

$$1.238 \qquad 1.507 \qquad 97$$

In cases where no decomposition of the salt occurs, the method gives results too high, as, for example, 78.6 instead of 69, for sodium nitrite; but taking into consideration the partial hydrolysis of the hyponitrite that certainly takes place, its molecular weight is clearly indicated as 106 rather than 53.

Constitution.—The constitution (HNO)₂ seems to be excluded by considerations of valency, but the positive evidence for (HON)₂ is ample. Zorn's observation that ethylic hyponitrite decomposes into nitrogen and alcohol (and aldehyde), even in presence of reducing agents, establishes the diazo-grouping in hyponitrites. Ammonia or other amine is never produced in the decomposition of any hyponitrite. Then the conversion of a hydroxyamidosulphonate into hyponitrite affords a beautiful demonstration of the oxylic constitution of the hyponitrites,

2HO·NH·SO₃Na+4NaOH = NaON:NONa+2NaSO₃Na+4H₂O. Hantzsch and Sauer have also given an equally convincing proof of the same point, by introducing nitrosyl into dimethylhydroxycarbamide and decomposing the product by alkali (see below). The facts that cuprous hyponitrite cannot exist, and, on the other hand, that the mercurous hyponitrite, and not the mercuric salt, is stable, point also to the metals being united to the oxygen, and not to the nitrogen.

Hantzsch and Sauer, in their desire to prove that nitramine is not $H_2N\cdot NO_2$, but a stereoisomeride of hyponitrous acid, would have it that their interesting formation of hyponitrous acid from dimethyl-hydroxynitrosocarbamide is analogous to that of nitramine from nitrosourethane,

 $EtO \cdot CO(N_2O_2H) + HOH = H(N_2O_2H) + EtO \cdot COOH ; \\ NMe_2 \cdot CO(N_2O_2H) + HOH = H(N_2O_2H) + NMe_2 \cdot COOH \text{ (decomposing)}. \\ However, by displaying what (N_2O_2H) conceals, namely, the difference between the nitramine and the isonitramine,$

Thiele. Hantzsch. EtO·CO·NH·NO₂, or EtO·CO·N
$$\bigcirc$$
N·OH + H₂O = NH₂·NO₂, or HN \bigcirc N·OH + &c.

 $NMe_2 \cdot CO \cdot N(OH)NO + H_2O = N(OH):NOH + &c.$

it becomes evident that the hydrogen of the water (or metal of the alkali) goes, in the case of the nitramine, to the amidic nitrogen united to the carbonyl, whilst, in the case of the isonitramine, it goes to the nitroxy- or nitroso-nitrogen not united to the carbonyl, even if Hantzsch and Sauer's free resort to tautomery could be justified. Surely, this difference is too great to allow of nitramine being treated as a probable or actual stereoisomeride of hyponitrous acid. Hantzsch's formula, KO·N—N·SO₈K, for potassium (hypo)nitrososulphate has been shown

by Haga and me to have nothing favouring its preference to that of KO·N:N·O·SO₈K, which has so much to be said for it.

Analogy of Hyponitrites to Carbonates—of N_2 to CO.—In hardly forming salts with the feebler metal radicles, such as aluminium and ferricum; in decomposing readily into anhydride and water; and in having its soluble normal salts with very alkaline reaction, hyponitrous acid resembles carbonic acid, as was indicated in my first paper. Zorn, also, in one of his papers, dwells on the analogy of the one acid to the other, pointing out that the salts have the same molecular magnitude, since N_2 and CO are both 28.

As is well known, the physical properties of nitrogen and carbon monoxides are throughout almost identical. The radicles, carbonyl and dinitrogen, also are both bivalent, and occur combined with oxylic, imidic, and alkyl radicles. Thus, $CO(ONa)_2$ and COONa(OH) find their analogues in $N_2(ONa)_2$ and $N_2ONa(OH)$. Just as ferric oxalate, $Fe_2(C_2O_2O_2)_3$, becomes $Fe_2(C_2O_2O_2)_2 + 2COO$, so $Hg_2(N_2O_2)_2$ becomes $Hg_2(N_2O_2) + 2NO$. COO corresponds with N_2O ; also CO:NAg to $N_2:NAg$. Lastly, ketonic compounds are perhaps represented by azo-compounds.

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XVI.—Derivatives of Camphoric Acid. Part III.

By FREDERIC STANLEY KIPPING, Ph.D., D.Sc., F.R.S.

THE first of these papers on derivatives of camphoric acid (Trans., 1896, 69, 913) contained an account of a number of optically active acids and other compounds which had been obtained from π -bromocamphoric acid, in the course of attempts to open the closed chain contained in this simple substitution product of camphoric acid at a different point from that at which it is broken in the oxidation of camphoric acid, the parent substance, to camphoronic acid.

The principal acids, which have already been described, were obtained in the following manner. π -Bromocamphoric acid was treated with an alkali and thus converted into (a) trans- π -camphanic acid,

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 $C_{10}H_{14}O_4$, a monocarboxylic acid containing a lactone ring, and (b) π -hydroxycamphoric acid, $C_{10}H_{16}O_5$; these two compounds were oxidised by nitric acid to one and the same trans- π -camphotricarboxylic acid, from which the cis-isomeride was also obtained.

The further oxidation of trans- π -camphotricarboxylic acid being attended with considerable difficulty, owing to the great stability of the compound, it was converted into its monobromo-substitution product and the latter was then decomposed with water; in this way, two isomeric lactones of the composition $C_{10}H_{12}O_6$, derived from a hydroxycamphotricarboxylic acid, $C_{10}H_{14}O_7$, were obtained, but these derivatives, like the parent substance, were found to be very stable, and could not be made to yield satisfactory oxidation products.

Having failed to obtain any easily oxidisable derivative of camphoric acid by these means, attempts were next made to oxidise cis- π -camphanic acid, $C_{10}H_{14}O_4$, an interesting compound obtained by the distillation of its isomeride trans- π -camphanic acid; these experiments were successful in a measure, inasmuch as a crystalline hydroxy-cis- π -camphanic acid was thus obtained, but this compound, like the others just mentioned, effectually resisted further oxidation.

It will be seen from this brief statement that the main object of this investigation had been defeated by the stability of these different substitution products of camphoric acid, all of which still contained the closed chain of the parent substance; moreover, the difficulty of obtaining material sufficient for oxidation experiments on the large scale rendered it almost impossible to proceed further on these lines. It was necessary, therefore, to try and attack the π -bromocamphoric acid in a somewhat different manner, namely, to convert it, if possible, into a dibromo-compound, and then to substitute hydroxyl for one, or both, of the bromine atoms, and thus obtain in a more direct manner a substitution product which might be oxidisable.

The results of these experiments are described in this paper.

When π -bromocamphoric acid is brominated, it is converted, in almost theoretical quantities, into a substance of the composition $C_{10}H_{12}Br_2O_3$, which, for reasons given later, is named πw *-dibromocamphoric anhydride; this substance crystallises in magnificent rhombic plates, and on hydrolysis with concentrated nitric acid it is transformed into πw -dibromocamphoric acid, $C_{10}H_{14}Br_2O_4$, a substance which in many respects is very similar to π -bromocamphoric acid and other halogen derivatives of this compound which have been described (compare Lapworth and Kipping, Trans., 1897, 71, 15).

 πw -Dibromocamphoric acid is decomposed when it is heated alone or with water, yielding hydrogen bromide and an acid of the composition

* The letter w has been previously used to denote a certain position in the molecule of camphoric acid (compare Trans., 1896, 69, 61, and 916).

 $C_{10}H_{13}BrO_4$, which, from its method of formation, must be regarded as a lactonic monocarboxylic acid; for this and other reasons, this compound is named π -bromo-w-camphanic acid. It crystallises in orthorhombic prisms, and both its amids, $C_9H_{12}BrO_2 \cdot CO \cdot NH_2$, and methylic salt, $C_9H_{12}BrO_2 \cdot COOMe$, are well-defined compounds.

When π -bromo-w-camphanic acid is treated with alkalis, it yields a crystalline product which is identical with hydroxy-vis- π -camphanic acid, the oxidation product of vis- π -camphanic acid; this hydroxy-acid is also formed by the action of excess of alkali on πw -dibromocamphoric anhydride. When, on the other hand, π -bromo-w-camphanic acid is boiled with nitric acid and silver nitrate, it is converted into a compound of the composition $C_{10}H_{12}O_{\psi}$, which is identical with one of the isomeric lactones of hydroxycamphotricarboxylic acid.

These transformations, the chemical properties of the various compounds, and the relations existing between these and other substitution products of camphoric acid, can only be elucidated by making use of some structural formula for camphoric acid, and in previous papers Bredt's formula was employed because it accounted for all the facts under discussion in a satisfactory manner, and at the same time seemed to have more evidence in its favour than any other of the many formulæ which had then been suggested. The recent publication of an important paper by W. H. Perkin, junr. (Trans., 1898, 73, 796), in which a new formula for camphoric acid is propounded, has certainly necessitated a modification of this last statement; nevertheless, the difference between Bredt's and Perkin's formulæ is of such a kind as to require little, if any, alteration in the views which have been advanced in explaining the relationship of these x-derivatives.

On inspection, it will be seen that these two formulæ, which are given below, differ merely in this; namely, that one of the >CH, groups in Bredt's is transferred, in Perkin's formula, to a position between the >CMe, and >CH·COOH groups.

This change does not effect any of the author's previous arguments, which were mainly based on stereochemical considerations, and, in fact, only makes this difference, that the π -camphanic acids, according to Perkin's formula, may, but do not necessarily, contain a δ - instead of a γ -lactone ring.

Making use, then, of Perkin's formula, and representing π -brome-camphoric acid by I (below), the substitution of bromine for hydrogen would afford a dibromocamphoric acid which must be represented by formula II, because in the formation of this substance the bromine doubtless displaces the same tertiary hydrogen atom as that which is expelled in the formation of w-bromocamphoric anhydride from ordinary camphoric acid.

$$\begin{array}{c|c} \operatorname{CH}_2 & \operatorname{CCH}_3 & \operatorname{CH}_2 & \operatorname{CCH}_3 \\ \operatorname{CH}_2 & \operatorname{CCH}_2 \operatorname{Br} \\ \operatorname{CH}_2 & \operatorname{CCH}_3 \\ \operatorname{CH}_2 & \operatorname{CCH}_3 \\ \end{array}$$

I. π-Bromocamphoric acid. II. πω-Dibromocamphoric acid.

π-Bromo-w-camphanic acid, which is formed from the dibromo-acid with the greatest readiness, just as w-camphanic acid is very easily produced from w-bromocamphoric acid, might be represented by one of several isomeric formulæ, of which, however, it is unnecessary to give examples, as it is possible to select the most probable one from a consideration of the following facts and arguments. In the first place, there are strong grounds for supposing that the z-bromine atom, namely, that which is a constituent of the -CH₂Br group, is still present in this bromocamphanic acid, because it is known that the w-bromine atom in w-bromocamphoric acid is very easily eliminated as hydrogen bromide by the action of boiling water, whereas x-bromocamphoric acid is comparatively stable under these conditions; in the second place, the bromocamphanic acid in question offers considerable resistance to the attack of oxidising agents, whereas had it been formed by the elimination of the π -bromine atom, it should resemble trans-x-camphanic acid in behaviour and be easily oxidisable to a bromo-tricarboxylic acid.

A comparatively simple way of settling this question as to which of the two halogen atoms is eliminated from the dibromo-acid offered itself, namely, to prepare a π-bromo-w-chlorocamphoric anhydride by chlorinating the π-bromo-acid, and then to convert this substance into the substituted camphanic acid by treatment with boiling water. On making these experiments, it was found that the π-bromo-w-chloro-camphoric anhydride, C₁₀H₁₂BrClO₃ was readily acted on by boiling water with formation of hydrogen chloride and a bromocamphanic acid identical with that obtained from the dibromo-aphydride. It follows, therefore, that the bromo-acid in question is a π-bromo-w-camphanic acid, and its constitution may be expressed by one of the following stereoisomeric formulæ.

$$\begin{array}{|c|c|c|c|c|c|} CH_2 & CCH_3 \\ CH_2 & CH_2Br \\ CH_3 & COOH \\ \hline \end{array}$$

III. #-Bromo-cis-w-camphanic acid. IV. #-Bromo-trans-w-camphanic acid.

Now it seems probable that the first of these two formulæ represents the configuration of the acid better than does the second, in spite of the fact that this view necessitates the assumption that intramole-cular change occurs in the formation of the acid from πw -dibromocamphoric anhydride; when the properties of ordinary w-camphanic acid are considered, it must be admitted that this compound is probably a cis-lactonic acid, because the hydroxy-acid, of which it forms salts on treatment with alkalis, is not known in the free state, but immediately passes into its lactone; w-camphanic acid, therefore, is doubtless stereochemically analogous to cis- π -camphanic acid, whereas the trans-w-camphanic acid, corresponding with the unstable trans- π -camphanic acid, has not yet been prepared.

It is probable, then, that when w-bromocamphoric anhydride is converted into w-camphanic acid, the carboxyl group changes its position stereochemically, just as it is known to do to a considerable extent in the reduction of w-bromocamphoric anhydride, a reaction which affords a mixture of cis- and trans-, or d- and d-iso-camphoric acids (Aschan, Acta Soc. Scient. fenn., 21, [v], p. 195).

The conclusion thus arrived at, namely, that π -bromocamphanic acid has the configuration represented by formula III, is in accordance with the behaviour of this substance, and also accounts for its conversion into hydroxy-cis- π -camphanic acid; when treated with potash, it may be supposed that it first gives a salt of w-hydroxy- π -bromocamphoric acid, the w-lactone ring undergoing hydrolysis, and that then potassium bromide is eliminated with formation of a different lactone ring, namely, that which is contained in cis- π -camphanic acid.

$$\begin{array}{c|c} \operatorname{CH}_2 & \operatorname{C} & \operatorname{CH}_8 \\ & \operatorname{CH}_2 & \operatorname{CH}_2 \operatorname{Br} \\ & \operatorname{CH}_3 & \operatorname{COOH} \\ \end{array}$$

$$\begin{array}{c|c} CH_2 & CCOOH \\ \hline CH_2 & CCOOH \\ CCOOH \\ COOH \\ CO$$

V. z-Bromo-cis-w-camphanic acid. VI. w-Hydroxy-cis-z-camphanic acid.

The last formula (VI) indicates the possible existence of a dilactons, which would be derived from hydroxy-cis-x-camphanic acid by the elimination of one molecule of water from the remaining -OH and

-COOH groups; although the isolation of such a substance has not yet been accomplished, indications of its formation have been observed, and the neutral crystalline compound obtained by brominating trans- π -camphanic acid (Trans., 1896, 69, 934), or the neutral oily product formed in the decomposition of πw -dibromocamphoric anhydride (see later), may possibly be a compound of this kind; it is by no means improbable, however, that the existence of one lactone ring may, owing to stereochemical causes, hinder the formation of a second one, and thus render it difficult to obtain such a dilactone by ordinary methods.

The further oxidation of the compounds obtained from dibromocamphoric anhydride has not yet been accomplished with satisfactory results in a single case; to give an instance of the difficulty of oxidising some of these products, it may be mentioned that a small quantity of the lactone of w-hydroxycamphotricarboxylic acid may be heated at 100° with a mixture of concentrated nitric and hydrochloric acids, or with a mixture of concentrated nitric and sulphuric acids, and after several hours treatment, the lactone is deposited unchanged on keeping the solution at ordinary temperatures.

Most of the compounds described in this paper are readily obtainable in well-defined crystals, and the author has again to express his thanks to Mr. W. J. Pope for a number of interesting reports on the crystallographic characters of the various substances which have been submitted to him for examination.

Part of the cost of this, and of all the other investigations on camphor derivatives, which have been published by the author, alone and in conjunction with Mr. W. J. Pope and Dr. A. Lapworth, has been defrayed by grants from the Royal Society, for which the author desires to express his thanks to the Government Grant Committee.

EXPERIMENTAL.

mv-Dibromocamphoric Anhydrids, $C_8H_{12}Br_2 < C_O^{CO} > 0$.

Dry π-bromocamphoric acid (Trans., 1896, 69, 924), which has been freed from α-nitro-απ-dibromocamphor by washing with chloroform, is ground up with about one-tenth of its weight of amorphous phosphorus, and gradually treated with bromine in a Würtz flask; when the first vigorous action has subsided, the flask is heated on a waterbath and the addition of bromine continued very slowly, so that the quantity added in the course of about 3 hours is approximately twice the weight of the acid taken. During this operation, the evolution of hydrogen bromide gradually slackens, but without ceasing entirely, and bromine also escapes in small quantities, so that the end of the

normal reaction is difficult to recognise. The excess of bromine having been expelled, the product, which consists of a red, crystalline mass, saturated with a red oil, is well agitated with successive small quantities of cold water, and then with a little cold dilute alcohol; these liquids remove most of the oily impurity, leaving a pale reddish or greenish crystalline product, the weight of which is rather greater than that of the original acid, the average yield amounting to about 90 per cent. of the theoretical. A small quantity of a crystalline bye-product is obtained from the alcoholic washings, but the examination of this substance is not completed.

The crude anhydride is very easily purified, without appreciable loss, by dissolving it in boiling chloroform, and precipitating the filtered solution with ether, repeating these operations if necessary; a sample thus purified and dried over sulphuric acid was analysed.

0.1779 gave 0.2307 CO₂ and 0.0643 H₂O. C = 35.36; H = 4.01. 0.1248 ,, 0.1426 AgBr. Br = 47.8. $C_{10}H_{12}Br_{2}O_{3}$ requires C = 35.29; H = 3.52; Br = 47.06 per cent.

Dibromocamphoric anhydride is readily soluble in boiling chloroform, from which it crystallises in large, transparent plates (see
below) melting at 209—210°*; it is also readily soluble in boiling
sthylic acetate, acetic acid, and cold acetone, moderately in cold
benzene, and sparingly in cold ether and alcohol. It sublimes readily
when heated in a test-tube, giving a solid sublimate of lustrous prisms.
It seems not to be acted on by boiling quinoline, from which it separates
again on cooling, but when heated with aniline it is vigorously
attacked; it dissolves in warm, concentrated, sulphuric acid with
evolution of hydrogen bromide, and on heating more strongly the
solution darkens in colour considerably.

Boiling water slowly converts the anhydride into bromocamphanic acid and hydrogen bromide, and a boiling solution of half a molecular proportion of sodium carbonate in dilute alcohol brings about a similar change; boiling alcoholic or aqueous potash in excess causes the elimination of both the bromine atoms with formation of the potassium salt of hydroxy-cis-x-camphanic acid or dihydroxy-camphoric acid. Fusion with potash at a moderately low temperature also results in the formation of a salt, from which w-hydroxy-cis-x-camphanic acid is liberated on the addition of a mineral acid, but other products appear to be formed in small quantities. When silver nitrate is added to a solution of the dibromo-anhydride in acetic acid, the separation of silver bromide soon commences, and after prolonged boiling w-hydroxy-cis-x-camphanic acid can be isolated from the solution; the y-lactone of hydroxy-camphotricarboxylic acid (Trans., 1896,

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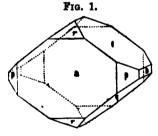
^{*} For corrections to be applied to these melting points, see Trans., 1897, 71, 963,

69, 961) also seems to be produced under these conditions by the oxidation of the dihydroxycamphoric acid, which is probably formed as an intermediate product, but the isolation of the lactone is not very easy.

Dibromocamphoric anhydride is leavorotatory. For the determination of its specific rotation, a solution in chloroform of 1.158 grams was diluted to 25 c.c., and examined at 14° in a 200 mm. tube; the mean of 7 observations gave $\alpha = -2.9^{\circ}$, from which $\lceil \alpha \rceil_{\rm p} = -31.2^{\circ}$.

The following is Mr. W. J. Pope's account of the crystals of the dibromo-anhydride, which were obtained by spontaneous evaporation of its solution in chloroform.

" πw -Dibromocamphoric anhydride crystallises in transparent, rhomboidal-shaped, orthorhombic plates (Fig. 1) possessing a calcite-like lustre. The dominant form is always the pinacoid $a\{100\}$, and the form $q\{011\}$ is usually the next largest; these two forms give fairly good reflections. The prism $p\{110\}$ is, as a rule, much smaller than $q\{011\}$, and the pinacoid $b\{010\}$ is generally very small; the form $r\{101\}$ is always small but bright, and is frequently absent.



- "Crystalline system.—Orthorhombic.
 - a:b:c=1.4844:1:0.7083.
- "Forms observed.— $a\{100\}$, $b\{010\}$, $p\{110\}$, $q\{011\}$, $r\{101\}$.
- "The following measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
ap = 100:110 $pp = 110:110$ $pp = 110:110$ $pp = 010:110$ $qq = 011:011$ $pp = 010:011$ $pp = 010:011$ $pp = 010:011$ $pp = 011:011$ $pp = 011:011$	34 18 29 24 29 37 18	55°44′— 56°17′ 67 81 — 68 12 83 80 — 84 24 109 1 —109 40 54 28 — 54 59 70 14 — 70 54 64 8 — 64 51 50 47 — 51 35	56° 2' 67 54 33 59 109 24 54 41 70 87 64 27 51 2	67°56′ 33 58 109 28 54 41 80″ 64 29 80 51 1

^{*} The polarimeter used in these determinations could only be read to 6', and ace the results may not be very accurate,

"The faces of the zone [001] are striated with lines parallel to the c-axis; these lines are sufficiently well developed as frequently to disturb the measurements in that zone. The optic axial plane is c(001), and the axis-b is a bisectrix of negative double refraction; the optic axial angle is very large, but the b-axis is probably the acute bisectrix. There is a fairly good cleavage on $a\{100\}$, and the cleavage faces are usually marked by the striations noted above; it is noteworthy that the crystals are always tabular on $a\{100\}$.

"After melting on a microscope slide under a cover slip in the usual way, the substance solidifies readily to a cubic modification; when the plate cools to about 60°, this changes to a doubly refracting biaxial modification made up of large individual fragments which, as cooling continues, crack across perpendicularly to their long directions. The pieces are frequently perpendicular to an optic axis, and are marked by interlaced straight striations. The double refraction seems to be of negative sign, and the modification is in all probability with the crystals measured above."

TW-Dibromocamphoric Acid, C₈H₁₂Br₂(COOH)₂.

It has been shown in previous papers that when an anhydride cannot be converted into the corresponding acid by treatment with alkalis or with boiling water, owing to elimination of the elements of a halogen acid, as, for example, in the case of the anhydrides of ω-bromocamphoric acid (Trans., 1896, 69, 1), π-bromocamphoric acid (Trans., 1896, 69, 927), and π-chlorocamphoric acid (Lapworth and Kipping, Trans., 1897, 71, 1), this conversion is easily accomplished by using concentrated nitric acid as the hydrolysing agent. This method can be applied with very satisfactory results for the preparation of dibromocamphoric acid from its anhydride.

Dibromocamphoric anhydride dissolves readily in hot, concentrated nitric acid (sp. gr. 1.4), and if the solution be cooled after heating during a few minutes only, most of the anhydride is deposited unchanged; if, however, the nitric acid solution be heated on a waterbath in an evaporating dish, crystals of the dibromo-acid begin to separate after a short time, neither nitrous fumes nor bromine being evolved in any appreciable quantity. When most of the nitric acid has evaporated, a little water is added to precipitate the rest of the dibromo-acid, and the colourless crystals are then separated and dried in the air. This product is generally free from anhydride, but should the latter be present, it is easily removed by washing the crystals with a little cold chloroform, in which the acid is insoluble, or nearly so.

For analysis, a sample was treated in this way, and then recrystallised from ether and dried at 100° until constant in weight.

0.1682 gave 0.2076 CO₂ and 0.0624 H₂O. C = 33.66; H = 4.12. $C_{10}H_{14}Br_{2}O_{4}$ requires C = 33.52; H = 3.91 per cent.

πω-Dibromocamphoric acid crystallises from ether, in which it is very readily soluble, in microscopic, four-sided plates; it dissolves freely in cold acetone, ethylic acetate, and methylic alcohol, but is almost insoluble in benzene as well as in chloroform. It melts at about 210°, effervescing, owing to the escape of water vapour and hydrogen bromide, and becoming slightly brown, but like ω-bromocamphoric acid and all the π-halogen derivatives of camphoric acid, it is stable at 100°, and does not lose in weight even after having been heated during several hours. It is practically insoluble in boiling water, although just sufficiently soluble to impart to the water an acid reaction after heating for a few minutes; it is probable, however, that the dibromo-acid does not dissolve unchanged, and that the acidity of the solution is due to hydrobromic and π-bromocamphanic acids, since these two compounds are rapidly produced when a solution of the dibromo-acid in dilute methylic alcohol is boiled.

Hot concentrated nitric acid dissolves dibromecamphoric acid freely, and on cooling beautiful, transparent, flat, four-sided crystals are deposited, but they are not large enough to be suitable for goniometric examination. The acid dissolves in dilute sodium carbonate, forming apparently the corresponding sodium salt, as on acidifying a freshly prepared solution with a mineral acid, dibromocamphoric acid is reprecipitated; when, however, such a solution of the acid is boiled for a few minutes and then acidified, crystals of π -bromocamphanic acid are deposited, hydrogen bromide having been eliminated.

When dibromocamphoric acid is heated in a test-tube over a small flame, it first melts with effervescence and then distils, charring very slightly but evolving hydrogen bromide, and apparently traces of carbonic anhydride; the crystalline distillate consists of a mixture of πw -dibromocamphoric anhydride and an acid melting at 176°, which is doubtless π -bromocamphanic acid.

No attempts were made to prepare salts of the dibromo-acid, on account of the readiness with which it is decomposed by water, alkali carbonates, and alkalis. It is interesting to note the relative stability of hot solutions of the acid in concentrated nitric acid and in water respectively; whereas the former may be heated during several hours without suffering any appreciable change, elimination of hydrogen bromide takes place rapidly in the aqueous solutions; this behaviour is similar to that of π -bromocamphoric acid,

π -Bromo-w-chlorocamphoric Anhydride, $C_8H_{12}BrCl < C_{CO}^{CO} > 0$.

The object of preparing this compound has already been stated; the method was the following. Dry powdered π -bromocamphoric acid was treated with a slight excess of the theoretical quantity of phosphorus pentachloride, the colourless liquid product heated on a water-bath, and dry chlorine slowly bubbled into it for about 4 hours, or until the evolution of hydrogen chloride almost ceased. The pale yellow oil thus obtained was gradually treated with ice cold water, whereon it quickly solidified, and was then purified by washing with water and dilute alcohol successively; for analysis, a sample was recrystallised twice from chloroform and then dried over sulphuric acid.

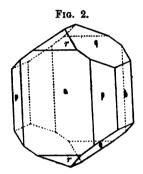
0.1576 gave 0.2349 CO_2 and 0.0602 H_2O . C = 40.65; H = 4.24. $C_{10}H_{12}ClBrO_4$ requires C = 40.62; H = 4.06 per cent.

π-Bromo-ω-chlorocamphoric anhydride, like the corresponding dibromo-compound, crystallises best from chloroform, from which it is deposited in lustrous prisms (see later) melting at 214—215°, or 5° higher than its analogue; a mixture of the dibromo- and chlorobromo-anhydrides shows no sign of melting until the temperature rises to 209—210°—the melting point of the former—an indication of the isomorphism of the two compounds which was confirmed by the crystallographic examination made by Mr. W. J. Pope (see p. 136).

In most respects, the properties of π -bromo-w-chlorocamphoric anhydride are so similar to those of the corresponding dibromo-compound that further description is unnecessary, but one rather interesting difference in behaviour may perhaps be noted. When the chlorobromo-compound is crystallised from a mixture of chloroform and ether, it is sometimes deposited in long, slender prisms, or needles, as well as in the compact prisms already referred to; these two kinds of crystals differ, not only in appearance, but also in behaviour, as the former become opaque when kept over sulphuric acid or heated on a waterbath, whereas the latter remain transparent; both forms, however, melt at $214-215^\circ$.

Experiments showed that the needles are formed when the crystallisation of the ethereal chloroform solution takes place at low temperatures, as, for example, at -5° , whereas, when the solution is kept at about the ordinary atmospheric temperature, one or other, or both forms may be deposited; ethereal chloroform solutions of the dibromo-anhydride, crystallised at temperatures just below 0° , did not deposit anything but the rhombic prisms described above. This anhydride, like the corresponding dibromo-compound, is levorotatory; a solution of 1.153 grams in chloroform diluted to 25 c.c., and examined at 14° in a 200 mm. tube, gave $\alpha = -2.4^{\circ}$ as the average of seven observations: hence $\lceil \alpha \rceil_{\rm p} = -26.1^{\circ}$.

" πw -Chlorobromocamphoric anhydride crystallises in large, transparent, orthorhombic prisms (Fig. 2), which appear rather more lustrous than the crystals of the corresponding dibromo-compound. The dominant form, as in the latter case, is usually the pinacoid $a\{100\}$, but the form $p\{100\}$ is sometimes the most developed; the pinacoid $b\{010\}$ is also usually well developed, and $q\{011\}$ is generally broader than in dibromocamphoric anhydride. The crystals of the latter give much better results on measurement than do those of the compound now described.



[&]quot;Crystalline system.—Orthorhombic.

a:b:c=1.4789:1:0.7107.

[&]quot;The following measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$ap = 100:110$ $pp = 110:\bar{1}10$ $bp = 010:110$ $qq = 011:01\bar{1}$ $bq = 010:011$ $qq = 011:0\bar{1}$ $ar = 100:101$	47 82 21 88 43 44	55° 1'— 56°54' 67 49 — 69 2 33 20 — 34 48 108 42 —109 57 53 39 — 55 10 69 57 — 71 28 63 19 — 65 6	55°56′ 68 31 34 7 109 16 54 38 70 48 64 24	68° 8′ 34 4 109 12 .54 36 — 64 20

[&]quot;The forms in the zone [001], and more especially the pinacoid $a\{100\}$, are marked with striations parallel to the c-axis. The optic axial plane is $c\{001\}$, and the axis b is the acute bisectrix; the double

[&]quot;Forms observed: $a\{100\}$, $b\{010\}$, $p\{110\}$, $q\{011\}$, $r\{101\}$.

[&]quot; Compare footnote, p. 132.

refraction is negative in sign, and the optic axial angle is large. There is a very poor conchoidal cleavage on $a\{100\}$.

"After melting on a microscope slide under a cover slip, the compound solidifies readily, yielding a singly-refracting cubic modification; this, before it cools to the atmospheric temperature, changes to a biaxial doubly-refracting modification, which is formed in large plates very similar to those constituting the film of the corresponding dibromo-derivative. These plates are marked with interlaced, straight striations, and are frequently perpendicular to an acute bisectrix of large axial angle and of negative double refraction.

"As would be expected from the chemical relationship between the two compounds, πw -dibromo- and πw -chlorobromo-camphoric anhydride are isomorphous; the axial ratios are of the same order and corresponding angles, as shown in the following table, do not differ greatly in the two cases.

,	C ₁₀ H ₁₂ Br ₂ O ₃ .	C ₁₀ H ₁₂ ClBrO ₃ .	Differences.
a/b	1·4844	1·4789	+ 0.0055
c/b	0·7083	0·7107	
a/c $ap = 100 : 110$ $bp = 010 : 110$	2·0958	2·0809	+0.0149
	56° 2′	55°56′	+0.6'
	33 58	84 4	-0.6
cq = 001:011 $bq = 010:011$ $ar = 100:101$	35 18 30"	35 24	-0530*
	54 41 30	54 36	+0530
	64 29 80	64 20	+0930
cr = 001:101	25 30 30	25 40	-0930

[&]quot;It will be seen that the dimensions measured in the zone [001] differ least in the two cases, whilst those in the parametral zone [010] exhibit the greatest differences. The same forms are present on crystals of both anhydrides and striations parallel to the zone axis observed in the zone [001] are also observed in both cases.

[&]quot;Amongst the differences may be noted that the crystals of the dibromo-compound show a much better cleavage parallel to $\{100\}$ than do those of the chlorobromo-derivative; again, the crystals of the former are really much better developed and give more trustworthy measurements than those of the latter substance. Further, there is a well-marked difference in habit. Crystals of the dibromo-anhydride are always tabular, whilst those of the chlorobromo-derivative are much more prismatic in habit; this is mainly due to a large development of the forms $p\{110\}$ and $b\{010\}$ on the latter crystals.

[&]quot;The behaviour of the two substances after melting and solidification is, in accordance with the isomorphism, extremely similar."

π-Bromo-w-chlorocamphoric Acid, C₈H₁₂BrCl(COOH)₂.

This acid can be prepared from its anhydride by the same method as that employed in the case of the dibromo-anhydride, namely, by dissolving the anhydride in concentrated nitric acid (sp. gr. 1·4), and then evaporating the solution on the water-bath. The colourless crystals of the acid are dried on porous earthenware, washed with a little chloroform to remove traces of unchanged anhydride which may be present, and then dried at 100°; for the analysis, a sample was recrystallised from ether, as the crystals retain small quantities of occluded nitric acid, which is not easily expelled even at 100°.

0.1689 gave 0.2395 CO₂ and 0.0693 H₂O. C = 38.67; H = 4.56. $C_{10}H_{14}BrClO_4$ requires C = 38.29; H = 4.46 per cent.

π-Bromo-w-chlorocamphoric acid is a microcrystalline, colourless powder, as prepared in the above manner; it melts at about 197° when heated fairly slowly from about 80°, effervescing vigorously, but as this temperature is a decomposition rather than a melting point, it varies a little with the rapidity of heating. There is, however, a much larger difference between the melting points of the bromochloro- and dibromo-acids, than between those of the corresponding anhydrides. In all ordinary properties, the bromochloro-acid resembles the dibromo-compound; it is, however, rather more soluble in boiling water, from which it separates in long, transparent prisms, which seem to contain water of crystallisation, as they become opaque when heated and melt at about 197°. It separates from cold concentrated nitric acid in nodular, opaque masses, and from ethereal chloroform in colourless, transparent, well-defined microscopic prisms; its behaviour towards boiling water is referred to later.

π -Bromocamphanic Acid, COOH·C $_8$ H $_{12}$ Br< CO .

Various methods can be adopted for preparing this compound from dibromocamphoric anhydride, or from the corresponding acid, some of which have already been mentioned. It may be obtained in large quantities by boiling the finely divided anhydride with a large volume of water, but as this process occupies a long time, owing to the slight solubility of the anhydride, the following method is more convenient.

The anhydride is dissolved in a small quantity of boiling acetic acid, and after adding a little water until a turbidity is just produced in the hot solution, the latter is heated on a sand-bath, more water

being added from time to time as the anhydride decomposes; during this process, the solution almost invariably acquires a distinct bright pink colour, which slowly changes to brown, the liquid then depositing traces of some tarry matter, doubtless due to impurity in the (crude) anhydride used. The hot solution is finally filtered, and on cooling the π -bromocamphanic acid is deposited in almost colourless needles; further quantities are obtained on evaporating the mother liquors, the yield being practically theoretical.

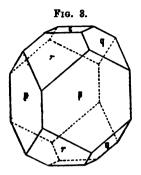
For analysis, a sample was purified by recrystallisation from a mixture of ethylic acetate and chloroform and dried at 100°.

0.1576 gave 0.2518 CO₂ and 0.0697 H₂O. C = 43.57; H = 4.91. $C_{10}H_{18}BrO_4$ requires C = 43.32; H = 4.69 per cent.

**Bromocamphanic acid usually separates from hot water, in which it is only moderately easily soluble, in small, well-defined, lustrous prisms, which do not lose in weight at 100°. It is comparatively sparingly soluble in boiling benzene, and only moderately so in boiling chloroform, but it dissolves readily in acetic acid, alcohol, and ethylic acetate; it crystallises best from cold, dilute acetic acid, from which it is deposited in transparent prisms described later. It melts at 176—177° without decomposing, but when heated at its boiling point it darkens considerably and seems to give off a little hydrogen bromide; the distillate soon crystallises on cooling, and consists of slightly impure bromocamphanic acid.

z-Bromocamphanic acid is a very stable substance in many respects, and boiling nitric acid, dilute or concentrated, does not oxidise any appreciable quantity of it in the course of a few hours. Prolonged boiling with a solution of chromic anhydride and dilute sulphuric acid seems to result simply in the elimination of hydrogen bromide, the bromocamphanic acid being converted into hydroxy-cis-π-camphanic acid; the last-named compound is also formed when the bromo-acid is boiled with an aqueous solution of silver nitrate, but other substances are also produced. When the acid is treated with ammonia under suitable conditions, a product is obtained which is almost insoluble in water, but which has not yet been analysed or examined.

Mr. Pope's description of this substance is as follows. "The crystals of bromocamphanic acid are very beautiful, transparent, orthorhombic prisms (Fig. 3), which have a very brilliant, glassy lustre. The prism $p\{110\}$ is always dominant, but gives poor results on measurement owing to the presence of vicinal faces and of striations parallel to the c-axis; the forms $q\{011\}$ and $r\{101\}$ are next in size, $r\{101\}$ being usually rather the larger, and give very brilliant reflections, so that the measurements obtained from them may be relied upon. The pinacoid $c\{001\}$ is very small and frequently absent.



"Crystalline System.—Orthorhombic.

a:b:c=1.4654:1:0.9501.

"Forms observed.— $c\{001\}$, $p\{110\}$, $q\{011\}$, $r\{101\}$.

"The following angular measurements were obtained.

Angle.	Number of measure-ments.	Limits.	Mean.	Calculated.
cr=001:101	9	85°17′— 85°59′	85°41′	85°89′30″
$rr = 101 : \overline{1}01$	29	71 12 — 71 26	71 19	_
$m = 101 : 10\overline{1}$	25	108 34 —108 48	108 40	108 41 8
pq = 110:011	84	70 41 — 70 56	70 49	
qr = 011:101	29	55 49 — 56 15	56 59	56 57
rp = 101:110	81	58 5 58 24	58 15	53 14
$qq = 011 : 01\bar{1}$	16	86 52 - 87 20	87 4	87 8
$qq = 011 : 0\bar{1}1$	14	92 37 — 98 11	92 55	92 52
cq = 001 : 011	15	46 1 46 54	46 21	46 26
pp = 110:110	37	110 47 —111 58	111 26	111 23
$pp = 110 : \bar{1}10$	24	68 20 — 69 18	68 47	68 37

"The plane c(001) is the optic axial plane, and an optic axis emerges obliquely through each face of the form $p\{110\}$; the double refraction is strong and the optic axial dispersion slight. After melting, the substance solidifies readily, and is thus obtained in large individual flakes, which are often marked by strise crossing each other at about 60° , and cracked across their longest dimension on cooling; the flakes are frequently perpendicular to an optically negative bisectrix of a large axial angle."

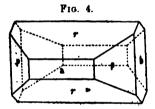
This ethereal salt is conveniently prepared by passing hydrogen chloride into a solution of the acid in methylic alcohol and then

evaporating at the ordinary temperature; the product, which is slowly deposited in felted needles, can be purified by recrystallisation from a mixture of ether and chloroform.

0.1662 gave 0.2777 CO_2 and 0.0832 H_2O . C=45.57; H=5.56. $C_{11}H_{15}BrO_4$ requires C=45.36; H=5.15 per cent.

Methylic π -bromocamphanate crystallises from ether and from most other solvents in long, transparent needles melting at 87—88°; it is very readily soluble in cold chloroform, methylic alcohol, and boiling ether, but comparatively sparingly soluble in light petroleum. Massive crystals are easily obtained from a solution in a mixture of ether and chloroform, and a specimen of the compound thus obtained was examined by Mr. W. J. Pope, whose report is now given.

"The crystals of methylic bromocamphanate are transparent orthorhombic plates or prisms, possessing a high lustre (Fig. 4); the habit of the crystals varies considerably, those of prismatic habit are lengthened in the direction of the axis-a, and somewhat flattened in that of the b-axis, the dominant forms being $a\{100\}$ and $r\{101\}$; the tabular crystals are flattened on two parallel faces of the form $r\{101\}$. Very good results are obtained on measuring the crystals.



"Crystalline System.—Orthorhombic.

a:b:c=1.0977:1:0.6561.

"Forms observed.— $a\{100\}$, $b\{010\}$, $p\{110\}$, $r\{101\}$.

"The following angular measurements were obtained.

Angle.	Number of measure-ments.	Limits.	Mean.	Calculated.
ap=100:110 pb=110:010 ar=100:101 rr=101:T01 pr=110:101	18 12 24 16 7	47°84′—47°47′ 42 12 —42 27 59 0 —59 28 61 31 —61 50 69 39 —69 52	47°40′ 42 18 59 8 61 42 69 45	42°20′ ————————————————————————————————————

"There is a poor conchoidal cleavage parallel to $b\{010\}$, and the axis-b is the acute bisectrix; the optic axial plane is c(001), and the double refraction is positive in sign, and strong. The optic axial angle is fairly large and the optic axial dispersion is slight.

"The substance solidifies readily after melting on a microscope slide under a cover slip, giving large, individual flakes; most of these are nearly perpendicular to an optically negative bisectrix of a very large optic axial angle, and these are full of symmetrically arranged eggshaped bubbles and of intersecting striations. A few fragments are usually to be observed which show no bubbles or striæ; these are nearly perpendicular to the optically positive bisectrix of a fairly large optic axial angle. This modification is doubtless identical with the crystals measured above."

Methylic π -bromocamphanate is slowly attacked by concentrated aqueous ammonia at ordinary temperatures, and is thereby converted into a crystalline substance, which, judging by its melting point and other ordinary properties, is identical with the π -bromocamphanamide produced by the action of aqueous ammonia on πw -dibromocamphoric anhydride. This compound may now be described.

$$\pi$$
-Bromo w camphanamide, $NH_2 \cdot CO \cdot C_8H_{12}Br \stackrel{CO}{\longrightarrow} O$.

When finely divided πw -dibromocamphoric anhydride is left in contact with concentrated aqueous ammonia at ordinary temperatures, it slowly changes into a rather more bulky mass of small prisms, but without passing into solution to any noticeable extent; after keeping the mixture for about two days, the product is separated by filtration from the ammoniacal solution, which contains a small quantity of a readily soluble, crystalline, ammonium salt, washed with cold water, and recrystallised from dilute methylic alcohol. The substance obtained in this way is the amide of π -bromo-w-camphanic acid, and an analysis of it gave the following result.

0.1678 gave 0.2671 CO₂ and 0.0796 H₂O.
$$C = 43.41$$
; $H = 5.27$. $C_{10}H_{14}O_8BrN$ requires $C = 43.47$; $H = 5.07$ per cent.

The nature of this compound is further established by the fact already mentioned, namely, that it is formed on treating methylic π -bromocamphanate with aqueous ammonia, and also by its behaviour on hydrolysis; when boiled for a short time with concentrated hydrochloric acid, it is converted into a crystalline acid, which melts at $176-177^{\circ}$, and has all the properties of π -bromocamphanic acid.

π-Bromo-w-camphanamide crystallises from most solvents in lustrous, transparent needles or prisms melting at 161—162°; it is very readily

soluble in cold chloroform, acetone, ethylic acetate, acetic acid, and most other solvents, and it also dissolves freely in boiling water, but it is insoluble, or nearly so, in a cold dilute solution of sodium carbonate. It seems to be dimorphous, as the transparent crystals deposited from dilute methylic alcohol become opaque at about 140° when slowly heated, and do so at even lower temperatures when the tube containing them is rubbed gently.

Formation of π -Bromocamphanic Acid from π -Bromo-w-chlorocamphoric Anhydrids.—It was stated in the introduction that π -bromo-w-chlorocamphoric anhydride is decomposed by boiling water, giving hydrogen chloride, and an acid identical with the π -bromo-w-camphanic acid, prepared in a similar manner from πw -dibromocamphoric anhydride; this statement rests on the following experimental evidence.

When bromochlorocamphoric anhydride is boiled for some hours with diluted acetic acid, and the filtered solution then allowed to cool, a substance crystallising in colourless prisms is deposited; this compound, after having been purified, melted at 176—177°, and in appearance and other properties seemed to be identical with π-bromocamphanic acid. The great similarity between dibromo- and bromochloro-camphoric anhydrides, however, if repeated in the case of the bromo- and chloro-camphanic acids, might render the distinction between the two latter a matter of some difficulty; for this reason, it was necessary to make the following analysis, the results of which show that the decomposition product of the bromochloro-anhydride is really a π-bromocamphanic acid.

0.1572 gave 0.2521 CO_2 and 0.0679 H_2O . C=43.74; H=4.80. $C_{10}H_{18}BrO_4$ requires C=43.32; H=4.69 per cent.

Hydroxy-cis-n-camphanic Acid.

It has been shown in earlier papers that cis- π -camphanic acid is slowly oxidised by potassium permanganate in alkaline solution, being converted into a hydroxy-cis- π -camphanic acid, which is the lactone of a dihydroxycamphoric acid; this hydroxy-acid can be obtained in various ways from dibromocamphoric anhydride and its derivatives.

When, for example, dibromocamphoric anhydride is boiled for some time with alcoholic potash, or fused with potash at a moderate temperature, both the bromine atoms are removed, and hydroxy-cis- π -camphanic acid can be isolated from the product by methods which it is unnecessary to describe. Again, when π -bromocamphanic acid is heated with silver nitrate in aqueous solution, silver bromide is rapidly deposited, and an acid having all the properties of hydroxy-cis- π -camphanic acid can be obtained from the solution.

A number of experiments were made in the hope of isolating a

dihydroxycamphoric acid, or the corresponding dilactone; for this purpose, the dibromo-anhydride, dibromo-acid, and π-bromocamphanic acid, were separately treated with aqueous silver nitrate under various conditions; in nearly every case the product seemed to be a mixture of two or three organic compounds, and it was not easily separable into its components by fractional crystallisation or by other methods; hydroxy-cis-x-camphanic acid was isolated in almost every instance, and also a crystalline substance, which from its melting point and other properties was found to be identical with the y-lactone of hydroxycamphotricarboxylic acid. Further, in several experiments, small quantities of an oily product were obtained; this substance, when purified, was only sparingly soluble in boiling water (the other two products are readily soluble), and apparently insoluble in cold dilute sodium carbonate; it was vigorously attacked by hot concentrated nitric acid, being converted into the y-lactone of camphotricarboxylic acid. These observations seem to show the existence of a dilactone of dihydroxycamphoric acid amongst the products of the action of silver nitrate on the bromo- and dibromo-compounds in question.

Hydroxy-cis- π -camphanic acid is prepared far more easily by one of these methods than by the oxidation of cis- π -camphanic acid, and its investigation, as well as that of some of the other compounds related to it, is being continued; the crystals of this acid, obtained from an acetone solution, are of large size and suitable for goniometric examination.

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XVII.—a-Ketotetrahydronaphthalene.

By Frederic Stanley Kipping, Ph.D., D.Sc., F.R.S., and Alfred Hill.

The conversion of phenylpropionic chloride into a-hydrindone by the action of aluminium chloride under the conditions described by one of us in a previous communication (Kipping, Trans., 1894, 65, 680) is an example of intramolecular condensation by which an open- is converted into a closed-carbon chain; the reaction also provides by far the most convenient method yet known for the preparation of a-hydrindone, as, with due care, the yield is invariably very good, and phenylpropionic chloride itself can be obtained without any difficulty in almost unlimited quantity; this method of preparation was, therefore, made use of in later investigations of the derivatives of a-hydrindone (Kipping and Revis, Trans., 1897, 71, 238).

That such a reaction would be capable of more general application was, of course, extremely probable, but until quite recently no opportunity offered itself of putting this view to the test of experiment; now, however, the reaction is being tried with various substances, and in the present paper some of the first results of this work are described.

Taking the well-known synthesis of α -naphthol from phenyl- $\beta\gamma$ -crotonic acid by Fittig and Erdmann as an indication of the ease with which intramolecular condensation may occur in the case of a benzene derivative containing a suitable unsaturated side chain, it seemed very probable that a similar change might be brought about in the case of phenylbutyric acid, if the chloride of this acid were treated with aluminium chloride in a suitable manner; if so, the analogy between phenylpropionic and phenylbutyric acid would be complete, the one giving α -hydrindone, the other α -ketotetrahydronaphthalene.

$$\begin{array}{cccc} CH_2 & CH_2 \\ CH_2 & CH_2 \\ COCl & COCl & CH_2 \\ \end{array}$$

Phenylbutyric chloride.

a-Ketotetrahydronaphthalene.

Experiments showed that a-ketotetrahydronaphthalene is, in fact, formed by the action of aluminium chloride on phenylbutyric chloride under the conditions described below, but, so far, satisfactory yields have not been obtained, owing probably to the readiness with which the ketone, when once formed, undergoes further condensation of the ordinary type; a sufficient quantity of this substance, however, has been obtained to enable us to study its properties in some measure, and to prepare from it various crystalline derivatives.

a-Ketotetrahydronaphthalene is isomeric with, and closely related to, the β -keto-compound, which was first prepared by Bamberger and Lodter (Ber., 1893, 26, 1833) by the action of alkalis on "tetrahydronaphthylene chlorhydrin" (2:, 3-chlorhydroxytetrahydronaphthalene), and afterwards examined by Bamberger and Voss (Ber., 1894, 27, 1547). As far as can be judged, the two compounds resemble one another very closely in properties, and both show the ordinary general reactions of ketones; the semicarbazone, oxime, hydrazone, and parabromhydrazone of the a-keto-compound are described in this paper, the oxime and hydrazone of the β -ketone having been previously prepared by Bamberger and Voss (loc. cit.).

That the substance we describe as a-ketotetrahydronaphthalene really has this constitution is shown, not only by its method of formation and ketonic properties, but also by the fact that it can be indirectly converted into a base which seems to be identical with ac-tetrahydro-

a-naphthylamine; this base was first obtained by Bamberger and Bammann (Ber., 1889, 22, 951) by reducing tetrahydro-1:5-naphthylenediamine with sodium and amylic alcohol, and then eliminating the amido-group combined with the unreduced aromatic nucleus.

The conversion of α -ketotetrahydronaphthalene into this base was accomplished by first preparing the oxime, and then reducing the latter with sodium amalgam in acetic acid solution.

The study of this interesting ketone is being continued.

A portion of the expense incurred in this and in two earlier investigations of a similar kind (Kipping, Trans., 1894, 65, 680; Kipping and Revis, Trans., 1897, 71, 238) has been met by a grant kindly awarded by the Government Grant Committee of the Royal Society.

EXPERIMENTAL.

Preparation of Phenylbutyric Acid.—The preparation of a large quantity of phenylbutyric acid by the method which we employed is not a very easy task, but we were unable to find any process which appeared to be more suitable, recorded in the literature.

Starting with benzaldehyde, anhydrous sodium succinate, and acetic anhydride, we first prepared the mixture of phenyl-\beta_\gamma-crotonic and phenylparaconic acids under the conditions laid down by Jayne (Annalen, 1883, 216, 97), but instead of then separating these two compounds by dissolving out the phenyl-\(\beta_{\gamma}\)-crotonic acid with carbon bisulphide, we submitted the dried mixture directly to dry distillation under reduced pressure (about 30 mm.), whereby, as Jayne has already shown (loc. cit.), the phenylparaconic acid is decomposed into phenyl-By-crotonic acid and carbonic anhydride, a small quantity of phenylbutyrolactone being also formed from the phenyl-By-crotonic acid by an intramolecular change. The distillate, which solidifies on cooling to a brown, pasty, crystalline mass, was spread on porous earthenware to separate the phenylbutyrolactone and other oily impurities, and afterwards recrystallised from hot carbon bisulphide, from which the phenyl-By-crotonic acid was deposited in almost colourless needles; the last portions of this acid generally contain a little benzoic acid, this compound being always present in the original condensation product in large quantities; it is best removed by heating the mixture on a water-bath, the residue being again crystallised from carbon bisulphide.

The phenyl- $\beta\gamma$ -crotonic acid was thus obtained in colourless needles melting sharply at 86°, but the yield was always very poor, owing to the formation of tarry matter in the original condensation process.

For the conversion of this unsaturated compound into phenylbutyric acid, the pure acid was reduced with sodium amalgam in alkaline solution, and after precipitating with hydrochloric acid and filtering, the rest of the product was extracted with ether, and the whole purified by recrystallisation from this solvent; the acid then melted at $47-48^{\circ}$ as stated by Jayne (loc. cit.). We did not experience any difficulty in reducing the phenyl- $\beta\gamma$ -crotonic acid at ordinary temperatures, although, according to Jayne, prolonged treatment and warming are necessary.

Phenylbutyric chloride, C₆H₅·CH₂·CH₂·CH₂·COCl, is easily prepared by treating the dry, powdered acid with a slight excess of the theoretical quantity of phosphorus pentachloride at ordinary temperatures, a vigorous action immediately setting in; instead of separating the product from the phosphorus oxychloride by fractional distillation under reduced pressure, as in the case of phenylpropionic chloride (Trans., 1894, 65, 484), we merely heated the oil on a water-bath under diminished pressure until the oxychloride had volatilised, using the residual phenylbutyric chloride, which is sufficiently free from impurity, for the subsequent experiments.

Phenylbutyric chloride, as thus obtained, is a yellowish, mobile liquid, having a slight, but not very unpleasant, odour; when poured into water, it rapidly solidifies to crystals, which are only very slowly decomposed by cold water, and which do not immediately dissolve in a cold dilute solution of sodium carbonate.

Action of Aluminium Chloride on Phenylbutyric Chloride.

Experiments were made in order to ascertain the conditions under which the conversion of phenylbutyric chloride into a-ketotetrahydronaphthalene could be accomplished, and we commenced by employing very much the same method as in the case of a-hydrindone, the acid chloride, mixed with about four times its weight of light petroleum (b. p. 40—60°), being treated with its own weight of anhydrous aluminium chloride. Under these conditions, however, only a very slight reaction, if any, occurred, and even after heating on the waterbath during 30—40 minutes, the phenylbutyric chloride was found to be unchanged; on employing as diluent a sample of light petroleum boiling at 60—80°, the reaction was almost as sluggish as before, but with petroleum boiling at 100—110° a vigorous evolution of hydrogen

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chloride set in on heating, and in a short time the reaction abruptly ceased. An examination of the product from this last experiment showed that the yield of ketone was extremely small, most of the acid chloride having been converted into a pale brown resin. For this reason, a smaller proportion of aluminium chloride was employed in the later experiments, and the results appeared to be distinctly better.

The most satisfactory yield, so far, has been obtained by working in the following manner. Phenylbutyric chloride (5 parts) is dissolved in light petroleum (25 parts) boiling at 100—110°, aluminium chloride (4 parts) is added, and the mixture is rapidly heated on a boiling water bath in a flask provided with reflux condenser; after a very short time, hydrogen chloride is very rapidly evolved, and during this reaction the flask is repeatedly and vigorously shaken. At the end of about 10 minutes, or when the evolution of gas suddenly ceases, the contents of the flask are cooled and water carefully added; finally, the mixture is submitted to distillation in steam. The petroleum which passes over first contains only a small quantity of the ketone, the rest distilling over slowly with the steam and leaving in the flask a brown, oily, non-volatile substance, which, on cooling, solidifies to a brittle resin; the ketone is isolated by evaporating the petroleum and by extracting the aqueous portion of the distillate with ether.

The α -ketotetrahydronaphthalene obtained in this way as a pale yellow oil is probably slightly impure, and is further treated in the manner described below; the yield is by no means satisfactory, being at the most only about 10 per cent. of the theoretical, but it is probable that, as in the case of α -hydrindone, further experiments will lead to the discovery of some slight modification of the process which will give much better results.

The principal product of the reaction is the brown, brittle resin, referred to above; this substance is probably formed from a-ketotetra-hydronaphthalene by a condensation process similar to that which occurs in the case of "anhydrobishydrindone," or by the further action of phenylbutyric chloride on the ketone in presence of aluminium chloride. To obtain some information on this point, some of the resinous substance was oxidised with nitric acid, and it was found to be ultimately converted into phthalic acid; this fact seems to justify the above assumptions, and to indicate that if this secondary reaction could be prevented the yield of the ketone would be as good as in the case of a-hydrindone.

a Ketotetrahydronaphthalene,
$$C_6H_4 < CH_2 \cdot CH_2$$

When working with small quantities of a-ketotetrahydronaphthalene, the best method of purification is doubtless the following. The crude

oil is converted into its sparingly soluble semicarbazone in the manner described later, and after recrystallisation it is heated in a small Würtz flask with rather more moderately-concentrated hydrochloric acid than is required to combine with the semicarbazide; the semicarbazone is thus decomposed with regeneration of the ketone, which can be distilled off in a current of steam and extracted with ether. The addition of a little acetic acid, in which the semicarbazone is readily soluble, hastens the reaction. In this operation, there is no appreciable charring if the pure semicarbazone be employed, and the decomposition appears to be normal, as expressed by the following equation.

$$C_{10}H_{10}:N\cdot NH\cdot CO\cdot NH_2+H_2O=C_{10}H_{10}O+NH_2\cdot NH\cdot CO\cdot NH_2.$$

a-Ketotetrahydronaphthalene is a colourless, mobile, highly refractive liquid. It does not crystallise when kept for some days at ordinary temperatures, or when cooled to 0° , whereas the corresponding β -ketone solidifies when cooled, and melts again at 18° (Bamberger and Voss, *loc. cit.*); it does not seem probable that this difference in behaviour is due to the presence of impurity in the α -ketone, as the process just given appears to be a very satisfactory method of purification.

a-Ketotetrahydronaphthalene is specifically heavier than water at 15°, and is moderately easily volatile in steam. It has only a faint odour, recalling that of camphor, but when warmed it has a distinct odour of peppermint. It shows many of the ordinary reactions of a ketone, and yields crystalline products with hydroxylamine, phenylhydrazine, &c.; it does not appear to dissolve in, or to combine with, sodium hydrogen sulphite in aqueous solution, although the β -ketone forms a crystalline additive product with this reagent.

The ketone itself was not analysed, as its composition is established by its method of formation and properties, and by the analysis of the semicarbazone.

a-Ketotetrahydronaphthalene Semicarbazone, $C_{10}H_{10}: N\cdot NH\cdot CO\cdot NH_2$.

When the crude ketone, obtained by the method described above, is heated with semicarbazide hydrochloride and sodium acetate in aqueous alcoholic solution, the separation of an almost colourless, crystalline compound soon commences, and the reaction is completed by warming on the water-bath during about 2 hours; the hot solution is then diluted with water, allowed to cool, and the product separated by filtration, and washed well with cold water.

When purified by recrystallisation from hot alcohol and dried over sulphuric acid, it gave the following result. 0.1640 gave 0.3885 CO₂ and 0.0968 H₂O. C = 64.6; H = 6.6. $C_{11}H_{18}N_8O$ requires C = 65.0; H = 6.4 per cent.

a-Ketotetrahydronaphthalene semicarbazone crystallises from alcohol in long, transparent needles or prisms, usually forming aggregates of a rosette-like form; these crystals are distinctly yellow, their colour being almost as intense as that of quinone, but when in a fine state of division the substance appears almost colourless. The melting point is not very definite, for when heated moderately quickly the finely-divided substance melts at about 217°, but larger crystals only sinter at this temperature, and do not liquefy completely until about 220°, when effervescence sets in and the substance darkens slightly; on heating more strongly, a large quantity of gas is disengaged and a yellow liquid remains.

The semicarbazone is comparatively sparingly soluble in boiling chloroform and ethylic acetate, and apparently insoluble in water; it dissolves fairly easily in boiling alcohol and boiling acetone, and also in warm acetic acid, but it seems to be decomposed on boiling its acetic acid solution. As stated above, this compound may be conveniently employed in the purification of the ketone, as the latter is immediately regenerated on warming the semicarbazone with hydrochloric acid; it also affords the best means of detecting and identifying the ketone, the phenylhydrazone being far less suitable for such purposes.

a-Ketotetrahydronaphthalene Phenylhydrazone, C₁₀H₁₀:N·NHPh.

This compound is easily obtained by treating the purified ketone with phenylhydrazine acetate in dilute acetic acid solution in the usual manner, combination taking place spontaneously; after warming gently, water is added, and the product, which is precipitated as a thick, yellow oil, is washed well with cold water, and then dissolved in methylic alcohol. From this solution, the hydrazone separates, on spontaneous evaporation, in a crystalline condition, but if the warm solution be rapidly cooled, the compound is generally deposited as an oil. The crystals obtained from methylic alcohol and other solvents are massive, transparent, almost colourless six-sided and rhomboidal plates melting at 84—85°, at the same time effervescing and decomposing; they are readily soluble in most of the ordinary organic solvents, and dissolve comparatively easily even in boiling light petroleum, separating again, on cooling, in lustrous, transparent prisms.

The hydrazone is very unstable, and soon decomposes on exposure to light and air; its behaviour towards hydrochloric acid seems to be similar to that of the parabromo-derivative described below.

a-Ketotetrahydronaphthalene Parabromophenylhydrazone, $C_{10}H_{10}\text{:}N\cdot NH\cdot C_{6}H_{4}Br.$

The preparation of this substance from the purified ketone and parabromophenylhydrazine is carried out exactly as described in the case of the preceding compound, interaction taking place very readily; the almost colourless, oily product, which is precipitated on the addition of water, crystallises immediately when treated with a little methylic alcohol, and is easily purified with the aid of this solvent, from which it separates, on cooling, in long, colourless prisms, or in massive, transparent crystals.

It melts at 117—118°, when heated fairly quickly from about 110°, effervescing and decomposing, and it is readily soluble in cold ether, ethylic acetate, acetic acid, and benzene; it also dissolves in boiling light petroleum, but, on cooling, separates again almost completely in nodular aggregates of needles. It is more stable than the hydrazone, and does not change colour when exposed to light and air during several days.

Attempts to regenerate the ketone by distilling the parabrom-hydrazone with moderately concentrated hydrochloric acid were not successful; under these conditions, the bromhydrazone is converted into a crystalline compound, which is probably produced by a change analogous to that which occurs in the formation of "benzyleneindol" from the phenylhydrazone of a-hydrindone (compare Hausmann, Ber., 1889, 22, 2019; Kipping, Trans., 1894, 65, 494).

a-Ketotetrahydronaphthaleneoxime, C10H10:NOH.

On gently heating a solution of the purified ketone in dilute methylic alcohol with hydroxylamine hydrochloride and excess of potash, the separation of a crystalline compound soon commences, if the alcohol be sufficiently dilute, and on allowing the solution to evaporate on the water-bath, most of the product is deposited in colourless plates. It is easily purified by recrystallisation from dilute methylic alcohol, the lustrous, transparent, well-defined rhomboidal crystals thus obtained generally exceeding 10 mm. in diameter. It melts at $102.5-103.5^{\circ}$ without decomposing, and is very readily soluble in cold ether, chloroform, methylic alcohol, and most other solvents; it also dissolves freely in cold concentrated potash, but it is insoluble, or nearly so, in water.

Conversion of a-Ketotetrahydronaphthalene into Tetrahydro-anaphthylamine.

Although the method of formation of the ketone described above and the analysis of its semicarbazone left little room to doubt that it had the constitution assigned to it, we thought it would be interesting to try and convert it into one of the tetrahydronaphthalene derivatives of known constitution; for this purpose, experiments were made with the object of converting the oxime into the tetrahydro-anaphthylamine described by Bamberger and Bammann (Ber., 1889, 22, 951).

Attempts to reduce the oxime with sodium and moist ether were not successful; even after employing a large excess of sodium, a portion of the ethereal solution gave, on evaporation, crystals of the unchanged oxime, and a basic substance appeared not to have been formed; we, therefore, tried the action of sodium amalgam in warm dilute acetic acid solution, and found that reduction took place very After using the amalgam in considerable excess of the theoretical quantity, the acid solution was submitted to distillation with steam, but as no unchanged oxime passed over, the solution was rendered strongly alkaline with potash, and again submitted to steam A colourless, strongly basic oil, which was only moderately soluble in water, then collected in the receiver. This aqueous distillate, having been mixed with excess of hydrochloric acid and evaporated almost to dryness on the water-bath, left a considerable quantity of a salt which crystallised in needles or prisms, and was very readily soluble in water; the yield seemed to be practically theoretical.

In order to prove that this salt was the hydrochloride of tetra-hydro-a-naphthylamine, a portion of it was roughly dried at 100°, and then heated for a few minutes with excess of acetic anhydride; on subsequently cooling and adding water, the acetyl derivative of the base separated in colourless needles.

Bamberger and Bammann (loc. cit.) describe this acetyl derivative as crystallising from very dilute alcohol in felted masses of needles, and they give 148—149° as its melting point. The compound we obtained had these and all other properties mentioned by Bamberger and Bammann, except that it melted at 144—145°, and its melting point underwent no change on recrystallisation. As, therefore, there was this considerable difference in melting point, which is difficult to account for, further evidence as to the identity of our base was desirable.

For this reason, we prepared the platinochloride, a salt which is

immediately precipitated in yellow plates or prisms on the addition of platinic chloride to a solution of the hydrochloride of the base. This compound crystallised from water in long, flat, orange-yellow prisms, was readily soluble in hot water and cold methylic alcohol, and melted immediately at 140° when suddenly heated, thus indicating that it contained water of crystallisation; these properties agreed with those assigned to the platinochloride of tetrahydro-a-naphthylamine by Bamberger and Bammann, and our salt, like theirs, melted at 190°, decomposing and effervescing; the temperature at which the salt melts and decomposes varies, however, within very wide limits, according to the rate of heating, and on heating quickly the temperature can be raised to about 197° before liquefaction and decomposition ensue.

An analysis was, therefore, necessary to confirm the supposed identity of the two compounds.

0.4543 salt, dried over sulphuric acid, lost 0.0232 at 100°. $H_2O = 5.1$. 0.4311 anhydrous salt gave 0.1224 platinum. Pt = 28.4.

Calculated for $(C_{10}H_{18}N)_{2}$, $H_{2}PtCl_{6} + 2H_{2}O$, $H_{2}O = 4.87$ per cent. Calculated for $(C_{10}H_{18}N)_{2}$, $H_{2}PtCl_{6}$, Pt = 27.6 per cent.

On ignition, the salt gave off fumes having a strong odour of naphthalene.

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XVIII.—Production of Optically Active Mono- and Di-alkyloxysuccinic Acids from Malic and Tartaric Acids.

By Thomas Purdie, F.R.S., and William Pitkeathly, B.Sc., Berry Scholar in Science.

It has been shown in previous papers (Trans., 1898, '73, 287, 862) that the high optical activity of the ethereal malates and lactates, prepared from the respective silver salts, is due to the production of small quantities of the more active alkyloxy-derivatives, and Rodger and Brame (Trans., 1898, '73, 306) were consequently inclined to attribute the abnormally high rotation of the ethereal tartrates, which they prepared from silver tartrate, to a similar cause. On hydrolysing specimens of methylic tartrate, on the other hand, which had been prepared by this and by the commoner methods, they found that the products showed practically the same rotation, which sug-

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gested the possibility that the ethereal salts from the two different sources might be isomeric.

The object of the present research was to obtain further evidence of the production of alkyloxy-derivatives in the interaction of the silver salts of hydroxy-acids with alkyl iodides, and to find a modification of the reaction which might serve as a practical method for their preparation. We have, accordingly, made further experiments on the production of alkyloxysuccinates from silver malate, and, Mr. Brame having kindly left us to continue his work, we have examined the product of the action of isopropylic iodide on silver tartrate for di-isopropoxysuccinic acid. We find that this compound is actually produced, and conclude, therefore, that a similar reaction occurs, although probably to a smaller extent, when other alkyl iodides are We find further that the ethereal malates and tartrates can be readily alkylated by means of alkyl iodide in the presence of silver oxide, the reaction furnishing a convenient method of preparing the optically active mono- and di-alkyloxysuccinic acids from malic and tartaric acid respectively. The ethereal di-alkyloxysuccinates are highly active compounds, and their presence even in small quantity would account for the abnormally high rotation of the ethereal tartrates prepared from silver tartrate. Observations made on the metallic salts of diethoxysuccinic acid also explain the apparently anomalous results obtained by Rodger and Brame in the hydrolysis of methylic tartrate.

Action of Alkyl Iodides on Silver Malate.

In former experiments with ethylic iodide (loc. cit.), the crude distilled product of the reaction had always nearly the same rotation, -14° (l=1). We now find that, by modifying the conditions, a somewhat more active liquid is obtained, although in no case is the proportion of ethoxysuccinate produced large enough to admit of its being separated from the malate. Thus, by adding the iodide (3 mols.) gradually to the silver malate (1 mol.), the treatment being otherwise the same as before, a product was obtained which, without fractional distillation, gave the rotation $-15\cdot31^{\circ}$. Even when 2 mols. of iodide only were used and benzene added to moderate the action, conditions which should be unfavourable to the hydroxyl group being attacked, the ethoxysuccinate was formed as before, the ethereal salt obtained showing a rotation almost identical with that just quoted.

In attempting to prepare isobutylic malate by the silver salt method (Trans., 1896, 69, 824), the product was found to consist mainly of free acid, which, however, was not further examined at the time; as it seemed possible that this result might be due to the

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formation of isobutoxysuccinic acid, we have investigated the reaction more closely. The method employed was the same as before, but the free organic acid was removed from the product before distillation by allowing it to stand over potassium carbonate. In an experiment in which 92 grams of malate were added gradually to 167 grams of iodide, the yield of ethereal salt amounted to only 5 grams, and in another experiment, in which the order of mixture was reversed, the yield was still less. The free organic acid, which was isolated as in a previous similar case (Trans., 1898, 73, 299), gave, on heating with a solution of barium hydroxide, a large quantity of barium malate; when dried at 160°, it was found to contain 50.89 per cent. of barium, the calculated number being 50.93. The filtrate from this, on evaporation, left a less granular and more soluble salt, which analysis showed to be barium isobutoxysuccinate contaminated with some malate. Great difficulty was experienced in freeing the isobutoxysuccinic acid from malic acid. We found, finally, that although both barium salts are precipitated on boiling their aqueous solutions, the isobutoxysuccinate differs from the malate in redissolving readily when the solution cools, which enabled us to obtain the isobutoxysuccinate as a flocculent powder approximately free from malate. The results of the combustion of the substance, dried at 160°, were as follows.

```
I. C = 28.93. H = 4.08; Ba = 42.71 per cent.

II. C = 29.03. H = 4.05; Ba = 42.36 ,, ,,

C_8H_{19}O_5Ba requires C = 29.54; H = 3.69; Ba = 42.15 per cent.
```

In very dilute aqueous solutions (c=0.9132) at 13°, the salt showed the specific rotation -21.4°. The silver salt could not be obtained by precipitation. The sodium salt, prepared from the barium salt, gave in aqueous solution the specific rotation -27.8° (c=1.888), and, on analysis, was found to contain 19.46 per cent. of sodium, instead of the calculated number, 19.66. The rotations quoted are much higher than those of the corresponding malates, and are such as butoxysuccinates might be expected to exhibit.

The 5 grams of ethereal salt, mentioned above, contained a small proportion of isobutylic isobutoxysuccinate. This was evident from its high observed rotation, $-15\cdot28^{\circ}$ in a 100 mm. tube, that of the corresponding malate being only $-11\cdot60^{\circ}$ (Zeit. physikal. Chem., 1895), 17, 249), and was confirmed by the detection of barium isobutoxysuccinate in the product of hydrolysis. The quantity of substance was too small to admit of its being purified, but it showed a specific rotation nearly the same as that quoted above, namely, $-20\cdot81^{\circ}$ at 10° for $c=1\cdot538$. These observations show that the reaction between isobutylic iodide and silver malate does not follow the normal course,

but that the main product is free malic acid, produced probably by the decomposition of the iodide into isobutylene and haloid acid, and that a considerable quantity of isobutoxysuccinic acid is also formed.

Mr. J. C. Irvine was good enough to examine for us the action of secondary butylic iodide on silver malate, in the hope that this iodide, like isopropylic iodide, would yield a larger proportion of the alkyloxyacid. He obtained from the product only a small quantity of a very soluble barium salt of wax-like appearance which, although it could not be obtained quite pure, was evidently a barium butoxysuccinate. On combustion, it gave results approximating to the calculated numbers, and its specific rotation in dilute aqueous solution, -20.97°, was practically the same as that of the isobutoxysuccinate.

Action of Isopropylic Iodide on Silver Tartrate.

Isopropylic iodide was used in this experiment, previous results having shown that it is more prone than other iodides to the reaction by which the alkyloxy-acid is produced. Sixty-seven grams of silver tartrate (1 mol.) were gradually added to 134 grams of the iodide (about 4 mols.) previously diluted with an equal volume of benzene, and the mixture was treated as in previous similar experiments. After distilling off the bensene and unaltered iodide, and shaking the residual liquid with a solution of sodium carbonate, a small quantity of an oily, ethereal salt remained, which, as it was too dark coloured for polarimetric observation, was diluted with an equal bulk of alcohol and then examined in a 100 mm. tube. The observed rotation, about +25°, showed that the substance was far more active than any of the ethereal tartrates. A crude, syrupy acid, obtained from this by hydrolysis with potassium hydroxide, acidifying with sulphuric acid, and extracting with ether, showed the specific rotation +29° in about a 10 per cent. solution, an activity much exceeding that of tartaric acid. The barium and magnesium salts did not crystallise; the calcium salt was very soluble in cold water, but was precipitated as a crystalline powder on boiling its aqueous Estimations of calcium in the salt, dried at 130°, gave the results 14.77 and 14.82 per cent., the calculated percentage for calcium di-isopropoxysuccinate being 14.70.

The production of the alkyloxy-compound in the reactions, which have been described in this and previous papers, appears to be due to some of the ethereal salt of the hydroxy-acid, which is formed in the first instance, reacting further with alkylic iodide and unaltered silver salt with the formation of silver iodide, ethereal salt of the alkyloxy-acid, and free hydroxy-acid, which is always present in the product. The free alkyloxy-acid or its acid alkyl salt, which also frequently results from the reaction, may be produced from the normal alkyl

salt by water accidentally present, or by a reaction such as the following, in the case, for example, of silver malate and ethylic iodide, $OH \cdot C_2H_8(COOAg)_2 + 2EtI = OEt \cdot C_2H_8(COOEt) \cdot COOH + 2AgI$.

Consideration of the reaction in question suggested that the alkylation would probably be much more complete if the ethereal salt of the hydroxy-acid was first prepared and then treated with alkyl iodide in the presence of silver oxide, or other metallic oxide of a similar nature. Ethylic malate, ethylic iodide, and lead oxide gave a negative result, but the product obtained by heating the malate and iodide with mercuric oxide yielded, on distillation in a vacuum, an ethereal salt much more active than the original malate, the rotation having risen from -11.8° to -30.7° (l=1). A mixture of ethylic malate and isopropylic iodide reacted very vigorously with silver oxide, and gave an ethereal salt showing the rotation -30.5° . As these results indicated that the expected reaction had occurred, the action of ethylic iodide on ethylic malate and on ethylic tartrate in presence of silver oxide was examined in detail.

Preparation of Ethylic Ethoxysuccinate from Ethylic Malate.

The materials used were 52 grams of ethylic malate, the rotation of which was $a = -11.83^{\circ}$ ($l = 1, t = 6^{\circ}$), 86 grams of ethylic iodide. and 64 grams of dry silver oxide, these proportions being chosen on the assumption that the reaction occurs in accordance with the equation $OH \cdot C_2H_2(COOEt)_2 + 2EtI + Ag_2O = OEt \cdot C_2H_2(COOEt)_2 +$ EtOH + 2AgI. The mixture, which underwent an energetic reaction on being gently warmed, was afterwards heated for some time on a water-bath, then diluted with benzene, filtered,* and distilled under reduced pressure, when it yielded 43 grams of a liquid having a nearly constant boiling point, and showing the rotation -41.21° in a 100 mm. tube at 6°. Assuming that the liquid consisted of only ethylic ethoxysuccinate and malate, the rotation indicated the presence of about 60 per cent. of the former compound. the malate, the mixture was shaken repeatedly with a cold 10 per cent. aqueous solution of potassium hydroxide until the residual oil was reduced to about one-half its original weight. The oil, after being washed with water and dried with calcium chloride, was found on distillation to boil at the same temperature as ethylic d-ethoxysuccinate formerly prepared (Trans., 1895, 67, 972), namely, at 124° under a pressure of 10 mm., and its analysis gave the following results agreeing with the composition of that substance.

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The silver residues from these and the succeeding experiments were black and their composition remains to be examined.

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Found: I. C = 54.63; H = 8.68 per cent.

II. C = 54.79; H = 8.44 ,, ,,

Calculated: C = 55.05; H = 8.26 per cent.
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A determination of the specific rotation of the liquid at 6° gave the following result: $a = -56.85^{\circ}$, l = 1, $d = 6^{\circ}/4^{\circ} = 1.0501$, hence $[a]_{n} =$ -54.14°. The specific rotation of ethylic d-ethoxysuccinate from the active acid, which was obtained by resolution of the racemoid compound (loc. cit., p. 979), was +55.48°. The somewhat lower rotation now found is accounted for by the substance being contaminated with some ethylic fumarate, produced probably in the preparation of the ethylic malate. The specific rotation of an aqueous solution of 1-sthoxysuccinic acid, which was obtained by hydrolysing the ethylic salt, acidifying the product and extracting it with ether, was found to be $[n]_0 = -31.14^{\circ}$ (c = 8.0588, t = 7°), a number about 3° lower than that previously found, the discrepancy here being greater than in the case of the ethylic salts owing to the fumaric acid being chiefly contained in the crystallised portion of the acid which was used in the determination. For further comparison of the acids from the two sources, observations were made on the acid ammonium salt which could be freed by crystallisation from fumarate. A determination of the specific rotation of the hydrated salt in aqueous solution at 8° gave the following result: $a = -6.00^{\circ}$, l = 2, c = 10.0288, hence $[a]_0 =$ -29.91°. The value formerly found for similar concentration at 17° To obtain evidence of the purity of the compound, a was 28.46°. silver salt was made from it, and analysed with the following result.

Found: C = 18.90; H = 2.27; Ag = 57.76 and 57.69 per cent. $C_6H_8O_5Ag_2$ requires C = 19.15; H = 2.13; Ag = 57.45 per cent.

The yield of alkyloxysuccinic acid by the process which has been described would probably be increased by employing a larger proportion of alkyl iodide and silver oxide, in order to allow for the loss which is doubtless entailed by their partial direct interaction.

Preparation of Ethylic d-Diethoxysuccinate from Ethylic Tartrate.

Attempts have been frequently made to alkylate the alcoholic hydroxyl groups of tartaric acid, but without success. Perkin (Trans., 1867, 20, 155), by the action of ethylic iodide on ethylic monosodic tartrate, obtained an oil which he thought was probably ethylic monethyltartrate, but the later researches of Lassar Cohn (Ber., 1887, 20, 2003), Mulder (Rec. Trav. Chim., 1889, 8, 361) and Freundler (Bull. Soc. Chim., 1894, 11, 308) have shown that neither the sodium nor potassium derivatives of ethylic tartrate react in the usual way with alkyl iodides. The ethylic diethoxysuccinate which Michael and

Bucher (Ber., 1896, 29, 1792) found to be one of the products of the action of sodium ethoxide on ethylic dibromosuccinate and on ethylic acetylenedicarboxylate, was shown by these authors to be the unsymmetrical compound.

The proportions of ethylic iodide and silver oxide employed in our experiments were 6 mols. of the iodide and 3 mols. of the oxide to 1 mol. of the tartrate, that is to say, an excess of one-half over the calculated quantity, assuming the reaction to proceed in the sense indicated in the case of ethylic malate. On adding the oxide to the mixture of iodide with tartrate, the reaction set in spontaneously, and became so violent that it had to be moderated by cooling. The liquid product, obtained as described under ethylic ethoxysuccinate, was about equal in quantity to the tartrate employed, its boiling point was nearly constant, and its observed rotation varied in different preparations from +83.5° to +92.5° in a 100 mm. tube. As the percentage numbers found, on analysis, were somewhat lower than those calculated for ethylic diethoxysuccinate, and as it proved impossible to purify the substance either by fractional distillation or by shaking with water, which we expected would remove unaltered ethylic tartrate, if present, we had to resort to the method of partial hydrolysis by shaking with a 10 per cent. aqueous solution of potassium hydroxide. The process entailed a considerable loss of material, but the residual oil, on redistillation (b. p. 149-151° at 15 mm.), had increased in rotation to +97.5°, and on analysis gave results in agreement with the calculated numbers.

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Found: I. C = 54.99; H = 8.71 per cent.

II. C = 54.87; H = 8.67 , ,,

Calculated for C_{12}H_{22}O_6: C = 54.96; H = 8.40 per cent.
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The specific rotation of the liquid at 18° was as follows: $a = +97.52^{\circ}$, l=1, d 18°/4°=1.0460, hence $[\alpha]_D = +93.23^{\circ}$. The ethereal salt of lower activity, which was removed by the partial hydrolysis, gave an uncrystallisable acid, which we intend to examine further.

d-Diethoxysuccinic acid, which was obtained from the ethylic salt in the same manner as the monethoxy-acid, is sparingly soluble in benzene, readily soluble in ether, alcohol, chloroform, and water, from which it crystallises in long prisms melting at 126—128°. The results of the analysis of the substance, dried at 100°, were as follows.

```
Found: I. C = 46.86; H = 7.04 per cent.

II. C = 46.81; H = 6.90 ,, ,,

Calculated for C_8H_{14}O_6: C = 46.60; H = 6.80 per cent.
```

The acid showed the following specific rotations in aqueous solu-

tions at 20°: a = +6.73, c = 10.1488, l = 1, hence $[a]_n = +66.31^\circ$; $a = +2.70^\circ$, c = 4.0595, l = 1, hence $[a]_n = +66.51^\circ$.

The silver salt is soluble in water, and does not decompose much on evaporating the solution. An estimation of silver in the salt gave the result 51·01 per cent., the calculated number being 51·43. The acid potassium and acid ammonium salts are crystalline. The normal sodium salt, in aqueous solution at 17°, showed the specific rotation +41·11° (c=3·138); the residue left on evaporating the solution, dried at 120°, was found to contain 18·35 per cent. of sodium instead of the calculated number, 18·40. The calcium salt is very soluble, and was not obtained in the crystalline state. The barium salt, which is characteristic, is sparingly soluble in cold water, and crystallises readily in large, glassy prisms, containing apparently 4H₂O, which is lost at 120—130°. Analysis of the anhydrous salt gave the following results.

Found: C = 27.78; H = 3.77; Ba = 39.94 and 40.12 per cent. Calculated: C = 28.15; H = 3.52; Ba = 40.18, ,

An aqueous solution of the salt at 16° had the specific rotation $+26\ 25^{\circ}$ (c=1.8092).

Ethylic d-diethoxysuccinate is also obtained by the direct action of ethylic iodide and silver oxide on tartaric acid, but the yield is smaller than when the alkyl tartrate is used as the starting point. From 17 grams of tartaric acid we obtained in this way 12 grams of an ethereal oil having the same boiling point, and the same observed rotation, $+85^{\circ}$, as the crude ethylic diethoxysuccinate prepared from ethylic tartrate.

The optical effect of the replacement of the alcoholic hydrogen of tartaric acid by alkyl radicles is of the same nature as that which attends a similar substitution in lactic and malic acids; the sign of rotation, defined in the case of lactic acid as that of its salts, remains unchanged; a striking rise of activity, observable more particularly in the free acids and the ethereal salts, is produced, and the specific rotation of the acids in aqueous solutions of varying concentration becomes more constant. Thus, in passing from tartaric to diethoxysuccinic acid the molecular rotation of the ethylic salt is raised from +15.8° to +244.3°, and that of the free acid at similar concentration from +20.6° to +136.6°. The ionic rotation, however, does not experience a proportional rise, the result being that, whilst in the case of the three hydroxy-acids mentioned the molecular rotations of the alkali salts in dilute solution greatly exceed those of the free acids, these rotations become nearly equal in the case of the alkyloxypropionic compounds, and the order of their value is reversed in the case of the mono- and di-alkyloxysuccinic compounds.

Our observations furnish a satisfactory explanation of the apparently anomalous results obtained by Rodger and Brame, which have been already referred to. An admixture of 6 per cent. of ethylic d-di ethoxysuccinate would suffice to account for the high rotation of the ethylic tartrate which they prepared by the silver salt method, but the difference between the rotations of the products of hydrolysis of such a mixture and of pure ethylic tartrate respectively would not, under the conditions of the experiment described by them, amount to more than 0.1—0.2°.

The action of alkyl iodides and silver oxide on the alkyl salts of optically active hydroxy-acids furnishes a general method of obtaining the active alkyloxy-acids. We have used the method with success for the preparation of alkyloxypropionic and alkyloxyphenylacetic acids from active lactic and mandelic acids, and we are at present studying the application of the alkylating agent to the alkyl tartrates in general and to other compounds.

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XIX.—Determination of the Constitution of Fatty Acids. Part I.

By ARTHUR WILLIAM CROSSLEY and HENRY RONDEL LE SUEUR.

Some short time ago one of us, in conjunction with Professor Perkin (Trans., 1898, 73, 1), described an investigation of a complicated mixture of fatty acids derived from the fusion of camphoric acid with alkalis; as the difficulties encountered in identifying some of the fatty acids were very great, it was considered desirable to try and devise a method for the determination of the constitution of such acids, and the object of this paper is to give a short account of experiments which have been carried out in this direction.

So far as our present experiments go, we think they may be described as satisfactory, and although the method may not be an infallible one, it seems likely to prove of considerable importance as a means of establishing the constitution of organic acids.

The method of procedure which was suggested to us by Professor Perkin is the following. Starting with a fatty acid, X·CH₂·CH₂·COOH, this is first converted into the ethylic salt of the monobromo-derivative by Volhard's process (Annalen, 1887, 242, 61); from the work of

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^{*} The experiment referred to was made on the methylic tartrates, but this would not materially alter the result as stated above.

Auwers and Bernhardi (Ber., 1891, 24, 2209) and others, there can be no doubt that, under these conditions, the bromine atom takes up the α-position, yielding the substance X·CH₂·CHBr·COOEt. The brom-ethereal salt is then treated with quinoline or diethylaniline (compare Weinig, Annalen, 1894, 280, 253), whereby the elements of hydrobromic acid are removed, and the ethylic salt of an unsaturated acid of the acrylic series, X·CH:CH·COOEt, is produced. The free acid obtained from this salt by hydrolysis is then oxidised, first with potassium permanganate, giving rise to the corresponding dihydroxy-acid, X·CH(OH)·CH(OH)·COOH, and then with chromic acid, when the molecule is broken down at the position occupied by the double bond in the unsaturated acid, giving X·COOH and COOH·COOH.

The result is, therefore, the production of oxalic acid and a fatty acid (or ketone) containing two carbon atoms less than the original acid, and as the number of isomerides decreases greatly with loss of two carbon atoms, the possibility of identification is much enhanced.

We have carried out this process with three acids, namely, valeric, iso-valeric, and iso-butylacetic acids, as we considered that the oxidation products of the acids of the acrylic series corresponding with these fatty acids would be typical examples of what might be expected to be met with in actual determinations. Thus valeric acid gives ethylacrylic acid, and this, on oxidation, propionic acid (normal acid); iso-valeric acid gives dimethylacrylic acid, which then yields acetone (ketone); and iso-butylacetic acid gives iso-propylacrylic acid, and, on oxidation, iso-butyric acid (iso-acid).

With the three acids mentioned, the method works well. In all cases we have been careful to note the yields of substances obtained in the various stages, and there is here appended a tabulated list of results. The numbers express the percentage yields, and are referred, in the case of the unsaturated ethereal salt and acid, to the amounts theoretically obtainable from the brom-ethereal salt employed; and in the case of the "acid or ketone produced on oxidation," to the amounts theoretically obtainable from the unsaturated acid used.

Acid employed.	Brom- ethereal ethereal salt. Unsaturated ethereal salt.		Unsaturated acid.	Acid or ketone produced on oxidation.	
Valeric ac id	97·5 98·0	52·0 80·0 70·0	41·0 55—60 61·0	58·0 47·0 50·0	

The poor yield of unsaturated ethereal salt obtained from ethylic bromovalerate is accounted for by the fact that there is also produced a considerable quantity of some substance of higher boiling point, which is at present under investigation; and the comparatively small amount of the solid dimethylacrylic acid obtained from its ethylic salt is due to the fact that an oily substance is produced at the same time (see page 164). In no case was oxalic acid identified in the products of the reaction, nor could it be expected to resist the action of the strong oxidising agents employed.

We have experimented with both quinoline and diethylaniline, using them as reagents for the elimination of the elements of hydrobromic acid, and find that, with the lower fatty acids, the one gives quite as good results as the other, but with the higher fatty acids diethylaniline is to be preferred. For example, in the case of ethylic bromisobutylacetate, the 42 per cent. yield of ethylic isopropyl acrylate, obtained when using quinoline, was increased to 70 per cent. by employing diethylaniline. Quinoline always gives rise to tarry products, which are not easy or agreeable to work with, whereas diethylaniline does not; in the latter case, however, the substances require to be heated together for a much longer time, and it is very difficult to eliminate the last traces of hydrobromic acid. As, however, the unsaturated ethereal salts are subsequently heated with alcoholic potash, the latter objection is of no great moment.

We intend to further test the efficacy of the method by trying it on other acids, such as (a) stearic acid, and from preliminary experiments already made with this acid, it seems highly probable that the various reactions will take place as expected. The insolubility of the hydroxylated higher fatty acids in water may render the oxidation with chromic acid a difficult operation, in which case it will be of interest to see whether fusion with potash will serve a similar purpose.

(b) It will be noticed that, among the acids examined, none contain alkyl groups in the a-position. In such a case, as, for example, ethylisopropylacrylic acid, quite a new point is raised. This acid,

C₂H₅·CH(C₃H₇)·COOH,

still contains one a-hydrogen atom, and should, therefore, yield an a-brom-ethereal salt in the usual manner; but when the latter is treated with quinoline, there are two possible ways in which hydrobromic acid may be eliminated (compare Perkin, Trans., 1896, 69, 1466), giving rise to

$$\begin{array}{cccc} (CH_8)_2CH \cdot C \cdot COOH & (CH_3)_2C \cdot C \cdot COOH \\ CH & or & CH_2 \\ CH_5 & CH_8 \end{array}$$

Methyl-a-isopropylacrylic acid.

Dimethyl-a-ethylacrylic acid.

The study of the oxidation products of the unsaturated acid or acids produced would, therefore, be of special importance.

(c) The method may also prove to be applicable in the case of dibasic acids, and we propose to try it on pimelic (isopropylsuccinic) acid.

EXPERIMENTAL.

Acetone from Isovaleric Acid.

Instead of starting with isovaleric acid, the ethylic salt of a-bromisovalerate supplied by Kahlbaum was employed, which, on distillation, boiled constantly at 185—186°, and a bromine determination gave the following numbers.

0.2514 gave 0.2275 AgBr. Br = 38.50. $C_4H_8Br \cdot COOC_2H_5$ requires Br = 38.28 per cent.

Treatment of Ethylic a-Bromisovalerate with Quinoline.—Weinig (Annalen, 1894, 280, 253) has shown that diethylaniline may be used instead of alcoholic potash for the elimination of the elements of hydrobromic acid, and later Perkin and Goodwin (this Journal, 1896, 69, 1470) described experiments in which they employed quinoline for the preparation of dimethylacrylic acid from ethylic a-bromisovalerate. We have followed their instructions exactly, using 50 grams (1 mol.) of the brom-ethereal salt and 70 grams (2 mols.) of freshly distilled coal-tar quinoline; on fractionating the product, it was found to distil between 153° and 155° as a colourless oil of penetrating odour. The yield is 80 per cent. of the theoretical.

This ethereal salt is readily saponified by alcoholic potash, and the dimethylacrylic acid formed boils constantly at a temperature of 114° under a pressure of 40 mm. On standing, the distillate solidifies almost completely to a mass of needle-shaped crystals, which, after being freed from the mother liquor by spreading on a porous plate and recrystallisation from light petroleum (b. p. 60—80°), melted at 68.5—69°, and gave the following results on analysis.

0.1047 gave 0.2296 CO₂ and 0.0744 H₂O. C = 59.80; H = 7.90. $C_5H_8O_2$ requires C = 60.00; H = 8.00 per cent.

The yield of pure acid is from 55—60 per cent. of the theoretical obtainable from the brom-ethereal salt employed. On extracting the porous plate just mentioned with ether, a small amount of an oily liquid was obtained which showed no signs of solidifying even after long standing, and which was not further investigated.

Perkin and Goodwin (loc. cit.) also mention this oily bye-product.

Treatment of Ethylic a-Bromisovalerats with Diethylanilins.—In using quinoline for the elimination of the elements of hydrobromic acid, there is always a considerable quantity of tarry matter formed, and in later experiments we found that diethylaniline could be used with

advantage instead of quinoline; the yield of unsaturated ethereal salt is considerably increased, and no tarry products are produced, although the mixture requires to be heated for a much longer period. The yield of ethylic dimethylacrylate as obtained in the experiments just described is good, but we thought it of sufficient interest to try the effect of diethylaniline on ethylic a-bromisovalerate. The process was carried out exactly as described on page 166.

There is, however, in this case, no particular advantage to be derived, for the yield of ethylic dimethylacrylate is no higher than when quinoline is employed.

Oxidation of Dimethylacrylic Acid with Potassium Permanganate.—
Ten grams of dimethylacrylic acid were neutralised with potassium hydroxide and dissolved in 600 c.c. of water; the whole was stirred with a turbine, and maintained at 0° throughout the operation; a rapid current of carbonic anhydride was then passed in, and a cold solution of 12 grams of potassium permanganate in 400 c.c. of water gradually added from a tap funnel. After standing overnight, the liquid was filtered from precipitated manganese dioxide, and evaporated to a small bulk; no attempt was made to isolate the dihydroxy-acid produced, but the liquid was at once submitted to the process of:—

Oxidation with Potassium Dichromate and Sulphuric Acid.—For this purpose, the evaporated liquid was placed in a flask connected with a condenser, and, after warming to 70° on the water-bath, a solution of 30 grams of potassium dichromate in dilute sulphuric acid was slowly run in, the heating continued for eight hours, and the whole steam distilled. The distillate, which was slightly acid to litmus paper, was carefully neutralised with potassium hydroxide, and again steam distilled; on adding an alcoholic solution of parabromophenylhydrazine to the distillate, there was an immediate and copious precipitate, which was collected and dried on a porous plate. After recrystallisation from light petroleum (b. p. 80—100°), it was obtained as beautiful, shining scales melting at 94°. Bromine determinations gave the following results.

```
I. 0.2886 gave 0.2314 AgBr. Br = 34.09.

II. 0.1226 ,, 0.0998 AgBr. Br = 34.58.

(CH<sub>8</sub>)<sub>2</sub>C:N·NH·O<sub>6</sub>H<sub>4</sub>Br requires Br = 35.24 per cent.
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Although the figures obtained are not so good as might be desired, there can be no doubt that this substance is the parabromophenylhydrazine compound of acetone (compare Neufeld, *Annalm*, 1888, 248, 96), the ease with which it undergoes decomposition accounting for the lowness of bromine found.

The parabromophenylhydrazine compound obtained weighed 10.7 grams, whereas the amount theoretically obtainable from 10 grams of

dimethylacrylic acid is 22.7 grams; this is a 47 per cent. yield of the substance.

The residue from the steam distillation was examined for oxalic acid, after removing the chromium by the use of sulphurous acid and then boiling with excess of sodium carbonate. No traces of the acid were found, nor is this to be wondered at, as, when produced, it would at once be further oxidised to carbonic anhydride and water, in presence of the strong oxidising agent employed. This remark also applies to the other oxidations mentioned in this paper; in no case was any oxalic acid detected.

Propionic Acid from Valeric Acid.

Preparation of Valeric Acid.—This acid was prepared by the condensation of ethylic sodiomalonate and normal propylic iodide, and, after saponification, heating the propylmalonic acid so formed. It boiled constantly between 184° and 185° (uncorr.).

Bromination of Valeric Acid.—Forty-four grams of valeric acid were brominated with 135 grams of dry bromine and 4.5 grams of amorphous phosphorus in the usual manner, the product slowly poured into three times its volume of absolute alcohol, and the ethylic a-bromovalerate extracted with ether and distilled under diminished pressure. It boils constantly at a temperature of 110° (40 mm.), and is obtained in nearly theoretical amount (97.5 per cent.).

Treatment of Ethylic a-Bromovalerate with Diethylaniline.—Seventysix grams (1 mol.) of the brom-ethereal salt, and 115 grams (2 mols.) of diethylaniline, were heated in two portions in a flask attached to an air condenser and containing a thermometer, so that the temperature of reaction could be noted; this begins at about 175°, and the thermometer rises rapidly to 190-200°, at which temperature the whole was maintained for 6 hours. The product, when cold, was poured into excess of dilute hydrochloric acid, and extracted with ether, &c., but as it was found to contain bromine, it was again heated with diethylaniline (1 mol.) for 16 hours at 190-200°. After extracting in the manner just described, the ethereal solution was dried over calcium chloride, the ether distilled off, and the liquid residue fractionated; by this means, 24 grams of ethylic ethylacrylate were obtained boiling at 155-160°. This is only a 52 per cent. yield, which is accounted for by the fact that 12 grams of some substance of higher boiling point (270-280°) was also produced, the nature of which is at present under investigation.

Ethylic ethylacrylate is readily saponified by alcoholic potash, yielding ethylacrylic acid as a colourless, oily liquid, with pungent, characteristic odour, boiling at 195—197° under atmospheric pressure, and

showing no signs of solidification even when cooled to -14° . The yield of pure acid is 41 per cent, of the amount theoretically obtainable from the ethylic bromovalerate employed.

A portion of the acid was converted into the silver salt and analysed.

0.3510 gave 0.1834 Ag. Ag = 52.25. $C_5H_7O_2Ag$ requires Ag = 52.17 per cent.

Oxidation of Ethylacrylic Acid.—Fourteen grams of the acid were oxidised exactly as described on page 165, firstly, with 16 grams of potassium permanganate, and then with a solution of 45 grams of potassium dichromate dissolved in dilute sulphuric acid; the mixture was distilled in a current of steam, and the distillate, after neutralisation with potassium hydroxide, was evaporated to complete dryness, finally on the water-bath. The fatty acids obtained on distilling the residue with concentrated sulphuric acid were dried by standing for some time in contact with concentrated sulphuric acid, and then fractionally distilled. Eventually, nearly the whole of the acids boiled between 137° and 143°, and a portion boiling at 140° was converted into the silver salt and analysed.

0.1914, on ignition, gave 0.1144 Ag. Ag = 59.77.

0.2386 gave 0.1744 CO_2 , 0.0640 H_2O , and 0.1420 Ag. C = 19.92; H = 2.97; Ag = 59.51.

 C_2H_5COOAg requires C = 19.89; H = 2.76; Ag = 59.66 per cent.

The fraction boiling between 137° and 143° was then converted into the anilide by heating for 24 hours with twice its volume of pure aniline, and the solid product was repeatedly crystallised from light petroleum (b. p. 80—100°), from which it separates in white, glistening plates melting at 102—103° (compare Crossley and Perkin, Trans., 1898, 78, 34).

0.1814 gave 15.2 c.c. moist nitrogen at 21° and 762 mm. N = 9.56. $C_2H_5 \cdot CO \cdot NH \cdot C_6H_5$ requires N = 9.39 per cent.

These data prove conclusively that the acid produced by oxidising ethylacrylic acid in the manner described is propionic acid. The amount of propionic acid obtained was 5.5 grams, which corresponds with a 53 per cent. yield of the amount theoretically obtainable from the ethylacrylic acid used.

Isobutyric Acid from Isobutylacetic Acid.

Preparation of Isobutylacetic Acid.—This acid was prepared by the condensation of ethylic sodiomalonate with isobutylic bromide, and

subsequent distillation of the product, after saponification with alcoholic potash. The acid boiled at 198—200°.

Bromination of Isobutylacetic Acid.—Fifty-two grams of the acid, 4.8 grams of amorphous phosphorus, and 140 grams of dry bromine were treated in the usual manner. Ethylic a-bromisobutylacetate was obtained as a colourless, pleasant smelling liquid boiling at 115° under a pressure of 43 mm.

0.1530 gave 0.1295 AgBr. Br = 36.01.

 $C_5H_{10}Br \cdot COOC_2H_5$ requires Br = 35.87 per cent.

The yield of the ethylic salt was 93 per cent. of the theoretical.

Treatment of Ethylic Bromisobutylacetate with Quinoline or Disthylaniline.—Eighty-five grams of the bromethylic salt were treated in two portions with quinoline exactly as described on page 164, and the unsaturated ethereal salt was distilled, when 22 grams were obtained boiling at 168—169° at the ordinary pressure. As this is only 42 per cent. of the amount theoretically obtainable, the effect of diethylaniline on the brom-ethereal salt was tried, when the yield was increased to 70 per cent. It was, however, found exceedingly difficult to get rid of the last traces of halogen; and even after a third treatment with diethylaniline, the substance did not give good results on analysis. Possibly this is due to the presence of traces of halogen.

I. 0·1040 gave 0·2526 CO₂ and 0·0966 H₂O. C=66·23; H=10·31. II. 0·1570 , 0·3820 CO₂ , 0·1416 H₂O. C=66·36; H=10·02. C_5H_9 ·COOC₂H₅ requires C=67·60; H=9·86 per cent.

Perkin and Goodwin (Trans., 1896, 69, 1471) found that ethylic dimethylacrylate, prepared in a similar manner, did not give good results on analysis, but no explanation of the fact is offered.

When hydrolysed with alcoholic potash, the oily, unpleasant smelling liquid boiling at 169° is converted into isopropylacrylic acid, which is a colourless, oily liquid of exceedingly unpleasant odour, boiling at 133° (50 mm.); it does not solidify when cooled to -15° . The yield is 61 per cent. of that theoretically obtainable.

The silver salt is a white, amorphous, insoluble precipitate. On analysis, it gave the following numbers.

0.2536 gave, on ignition, 0.1232 Ag. Ag = 48.58. $C_6H_9O_2Ag$ requires Ag = 48.77 per cent.

Oxidation of Isopropylacrylic Acid.—Twenty grams of the acid were oxidised with 30 grams of potassium permanganate, and afterwards with 60 grams of potassium dichromate dissolved in dilute sulphuric acid, and worked up exactly as already described on page 165; after careful fractionation of the acid, the portion boiling at 153—154° was converted into the silver salt and analysed.

0.2044, on ignition, gave 0.1134 Ag. Ag = 55.47.

0.2154 gave 0.1900 CO₂, 0.0682 H₂O, and 0.1198 Ag. C = 24.10; H = 3.52; Ag = 55.61.

 C_sH_7 : COOAg requires C=24.61; H=3.59; Ag=55.38 per cent.

The remainder of the acid (b. p. 152—158°) was converted into the anilide which crystallised from light petroleum (b. p. 80—100°) in glistening, feathery needles melting at 104—105° (compare Trans., 1898, 73, 34).

0.1296 gave 10 c.c. moist nitrogen at 20° and 762 mm. N = 8.84. $C_aH_7 \cdot CO \cdot NH \cdot C_aH_5$ requires N = 8.59 per cent.

The acid (50 per cent. yield) produced by the oxidation of isopropylacrylic acid was, therefore, isobutyric acid, and the oxidation had taken place in the manner expected.

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XX.—Some Halogen Derivatives of Acetone Dicarboxylic Acid. Part I.

By FREDERICK W. DOOTSON, M.A.

THE extremely reactive nature of the hydrogen atoms of acetone-dicarboxylic acid, $CO(CH_2 \cdot COOH)_2$, has already been shown by a long series of experiments, but, so far, no attempt to replace them by halogens has been recorded. This is the more remarkable, since halogen substitution products could not fail to lend themselves to reactions which would yield derivatives not easily obtainable by other means. The present paper is intended as a preliminary note of investigations undertaken in this direction.

Acetonedicarboxylic acid in aqueous solution reacts readily with chlorine and bromine, evolving carbon dioxide, and yielding an oil which attacks the eyes, and which, from its general properties, is probably a mixture of the halide derivatives of acetone. The interaction of these halogens with the ethylic salt, however, proceeds smoothly and with but little decomposition, yielding ultimately ethylic tetrahalideacetonedicarboxylate.

Ethylic tetrachloracetonedicarboxylate is easily obtained by passing a stream of dry chlorine into ethylic acetonedicarboxylate; the latter, prepared by the action of hydrogen chloride on an alcoholic solution of the acid (Annalen, 1891, 261,177), is sufficiently good for the purpose without further purification. Hydrogen chloride is freely evolved,

and the liquid becomes hot; the operation is continued until chlorine is no longer absorbed, when the contents of the flask are found to have increased in weight by about 65 per cent., the reaction as it approaches completion being facilitated by heating on the water-bath. The heavy, pale yellow, oily product is fractionated under reduced pressure, when the greater part of the liquid distils over between 180° and 183° (16 mm. pressure); this fraction is nearly pure ethylic tetrachloracetonedicarboxylate. A readier method of purification is found in fractional crystallisation. On cooling in a freezing mixture, a nearly solid mass is obtained which, after being drained by the aid of the filter pump, is strongly pressed between folds of bibulous paper; the crystals thus obtained are practically pure.

Ethylic tetrachloracetonedicarboxylate is very soluble in ether, benzene, alcohol, chloroform, carbon bisulphide, and light petroleum, but insoluble in water. On recrystallisation from alcohol, it is obtained in large, lustrous, colourless, rectangular plates or leaves, which melt constantly at 30—30.5° (uncorr.).

```
0.3660 gave 0.4220 CO<sub>2</sub> and 0.0947 H<sub>2</sub>O. H = 2.87; C = 31.44. 0.3455 ,, 0.5860 AgCl. Cl = 41.87. C<sub>0</sub>H<sub>10</sub>Cl<sub>4</sub>O<sub>5</sub> requires C = 31.81; H = 2.94; Cl = 41.68 per cent.
```

Since all the hydrogen atoms of the acid radicle have been displaced by chlorine, the constitution of this substance is without doubt represented by the formula CO(CCl₂·COOC₂H₅)₂.

So far this ethereal salt has resisted all attempts to saponify it. Cold, dilute aqueous potash seems to be without action; aqueous soda or potash, on warming, liberates alcohol, but the acid at the same time decomposes with the formation of oxalic acid, recognised by the insolubility of the calcium salt in acetic acid, by a melting point determination (104° uncorr.), and by a titration of the crystallised acid. Sodium ethoxide in alcoholic solution behaves in a similar manner, whilst water, hydrochloric acid, and hydrobromic acid at 200° are without appreciable effect.

Action of Alcoholic Potash.—If a cold alcoholic solution of potash be slowly poured into an alcoholic solution of the ethylic salt, the contents of the flask being kept cold, no potassium chloride separates, but after a short time a copious crop of colourless crystals is obtained; these are exceedingly soluble in water, but only slightly so in alcohol. An analysis showed them to be the potassium salt of dichloromalonic acid (Conrad and Brückner, Ber., 1891, 24, 2993). The following numbers were obtained on analysis.

```
\begin{array}{lll} 0.2297 \ \ \text{gave} \ 0.1587 \ \ K_2 SO_4. & K = 30.98. \\ 0.2159 & ,, & 0.2480 \ \ \text{AgCl.} & Cl = 28.42. \\ & CCl_2(COOK)_2 \ \ \text{requires} \ \ K = 31.32 \ ; \ \ Cl = 28.42 \ \ \text{per cent.} \end{array}
```

The mother liquor from these crystals was diluted, acidified, and extracted with ether, and the ethereal solution washed with water, dried over calcium chloride, and evaporated, when a liquid with a strongly acid reaction was left. A consideration of the action of ammonia on ethylic tetrachloracetonedicarboxylate, described below, leaves no room for doubt that this liquid is dichloracetic acid. Hence the reaction that takes place is represented by the equation

$$OC(CCl_2COOC_2H_5)_2 + 3KOH = CCl_2(COOK)_2 + CHCl_2 \cdot COOK + 2C_2H_5 \cdot OH.$$

Action of Aqueous Ammonia.—Ethylic tetrachloracetonedicarboxylate dissolves readily in aqueous ammonia with evolution of heat, and, on standing, a bulky crop of large, colourless crystals separates, these, on being recrystallised several times from hot water, are obtained in thin, rhombic leaves or plates, which melt constantly at 204—205° (uncorr.), are very soluble in alcohol and hot water, and moderately in ether, light petroleum, and benzene. From the melting point, although this is somewhat higher than that found by Conrad and Brückner (loc. cit.), and on analysis, this substance was identified as dichloromalonamide.

0.2083 gave 0.1596 CO₂ and 0.0472 H₂O. C = 20.89; H = 2.51.

0.1464 , 20.4 c.c. nitrogen at 18° and 768 mm. N = 16.57.

0.1470 ,, 21.1 c.c. ,, 19.5° and 750 mm. N = 16.58.

0.1624 , 0.2740 AgCl. Cl = 41.75.

 $CCl_2(CONH_2)_2$ requires C = 21.08; H = 2.35; N = 16.40; Cl = 41.42 per cent.

The mother liquor from the dichloromalonamide, on concentration, yielded a crop of crystals which, after recrystallisation from hot water, were obtained in short, thick, colourless needles with ill-defined ends; these crystals, which are very soluble in alcohol and hot water, and moderately so in cold water, melted sharply at 98—99° (uncorr.). This, together with a nitrogen determination, was sufficient to identify them as dichloracetamide (Hantzsch and Zeckendorf, Ber., 1887, 20, 1309).

0.2000 gave 19.5 c.c. nitrogen at 17° and 762 mm. N=11.35. CHCl₂CONH₂ requires N=11.06 per cent.

From these results, it follows that the interaction of ethylic tetrachloracetonedicarboxylate and ammonia must be represented by the following equation.

$$\begin{aligned} \text{CO}(\text{CCl}_2\text{COOC}_2\text{H}_5)_2 + 3\text{NH}_8 &= \text{CCl}_2(\text{CONH}_2)_2 + \\ &\quad \text{CHCl}_2 \cdot \text{CONH}_2 + 2\text{C}_2\text{H}_5 \cdot \text{OH}. \end{aligned}$$

From the above experiments, it appears that tetrachloracetonedicarboxylic acid, if capable of existence at all, must be a very

unstable compound towards alkalis, and that the displacement of hydrogen atoms by chlorine exercises a remarkably modifying influence on the nature of the products of decomposition, whilst the chlorine atoms themselves show an unexpected degree of stability. An attempt to obtain condensation products by the interaction of the dipotassium derivative of ethylic acetonedicarboxylate and ethylic tetrachloracetonedicarboxylate in alcoholic solution was unsuccessful, there being no separation of potassium chloride even after long-continued boiling.

The action of bromine on ethylic acetonedicarboxylate is very similar to that of chlorine, hydrogen bromide being freely evolved and the liquid remaining almost colourless. After adding excess of bromine and heating for some time on the water-bath, the contents of the flask were shaken with dilute sodium carbonate solution until the colour was discharged, extracted with ether, and the ethereal solution washed several times with small quantities of water. After drying and evaporating the ether, a pale yellow oil was left, which became very viscid in a freezing mixture, but could not be obtained crystalline. The reactions of this oil, although not identical with, are very similar to those of ethylic tetrachloracetonedicarboxylate, and will be described in a future communication.

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XXI.—Action of Chlorosulphonic Acid on the Paraffins and other Hydrocarbons as a means of Purifying the Normal Paraffins.

By SYDNEY Young, D.Sc., F.R.S.

In a paper by Dr. F. E. Francis and myself on the action of fuming nitric acid on the paraffins and other hydrocarbons (Trans., 1898, 73, 932), it was mentioned that Aschan had recently observed (Ber., 1898, 31, 1801) that di-isopropyl and isopentane are rapidly attacked by chlorosulphonic acid at the ordinary temperature. Aschan expressed the intention of continuing this investigation, and we suggested that it would be interesting to know whether chlorosulphonic acid, like fuming nitric acid, acts less energetically on the normal paraffins than on isoparaffins and other hydrocarbons that contain a iCH-group.

It occurred to me that, if this were so, it was not improbable that chlorosulphonic acid might be a useful reagent for removing small quantities of isoparaffins and methyl derivatives of the polymethylenes from the normal paraffins separated by fractional distillation from

petroleum. I, therefore, wrote to Prof. Aschan to ask him whether he had made any observations in this direction; he informed me, in reply, that he was chiefly interested in the "mechanism" of the reaction, and that he wished to continue the investigation from this point of view himself, but he very kindly expressed his willingness that I should compare the behaviour of the normal and isoparaffins towards chlorosulphonic acid, and that I should make use of the reagent as a means of purifying the paraffins.

As a preliminary experiment, I took equal small quantities of pure normal hexane and of isohexane, and added to each about its own volume of chlorosulphonic acid. The difference in the action was exceedingly marked; the isohexane became warm, and in a few moments bubbles of gaseous hydrogen chloride were rapidly evolved; the normal hexane, on the other hand, did not rise perceptibly in temperature, and it was only after some time that hydrogen chloride was given off. After standing all night, the isohexane had entirely disappeared, but about half the normal hexane was still left; the chlorosulphonic acid had changed to a dark, tarry oil, much blacker and thicker in the case of isohexane.

Again, pure normal octane from octylic iodide was far less rapidly attacked than normal octane separated from American petroleum by distillation.

In order to find whether normal paraffins from petroleum could be purified by means of chlorosulphonic acid, specimens of normal heptane and of normal octane freed from aromatic hydrocarbons were treated with about one-fifth of their volume of the acid and left in contact with it for two or three days, until the reaction had ceased. The dark oil was in each case separated, and the remaining hydrocarbon was shaken repeatedly with strong sulphuric acid until, on dilution, the acid gave no turbidity with water. The hydrocarbon was washed with water, then shaken with caustic soda, and, lastly, with water again; it was dried with phosphorus pentoxide and distilled twice from an ordinary distillation bulb. The sp. gr. was then determined, and the treatment with chlorosulphonic acid repeated. There was not a sufficient quantity of either paraffin, and they were both too impure, to begin with, to allow of the treatment being continued until the sp. gr. had become constant, but the following table will show that the normal octane was obtained nearly pure and that considerable progress had been made in the purification of the normal heptane.

Normal Octane.

	Sp. gr. 0°/4°.	B. p. (760 mm.).
Pure from octylic iodide	0.71848	125·75°
Specimen from petroleum before	10.5401	collected between
Specimen from petroleum before treatment with chlorosulphonic acid	0.7421	$ \left\{ \begin{array}{l} \text{collected between} \\ 125 \cdot 2^{\circ} \text{ and } 127 \cdot 0^{\circ} \end{array} \right\} $
After first treatment	•	125·2 —127·3°
,, second ,,	0.7224	125·7 —126·1°
" third "	0.71956	125·75—125·95°

Normal Heptane.

	Sp. gr. 0°/4°.	B. p. (760 mm.).
Pure from Pinus sabiniana	0.70048	98· 45 °
Specimen from petroleum before treatment with chlorosulphonicacid	10.7400	$\begin{cases} \text{collected between} \\ 98^{\circ} \text{ and } 102^{\circ} \end{cases}$
treatment with chlorosulphonicacid	30.1402 1	98° and 102° }
After first treatment	0.7319	99.1—100.3°
" second "	0.7223	99·1— 99·6°

The normal heptane must have contained a little isoheptane and a large amount of methylhexamethylene, and the normal octane a little iso-octane and a larger quantity of, presumably, dimethylhexamethylene. The normal octane was less impure than the normal heptane, and there was more of it (about 50 grams before treatment with chlorosulphonic acid); it was, therefore, possible to carry the purification farther, and there can be little doubt that if the quantity had been larger the impurities might have been completely eliminated.

Miss Fortey has also found that impure hexamethylene from Galician petroleum, boiling at a somewhat lower temperature than the pure substance, and, therefore, containing methylpentamethylene and possibly some low boiling heptane, has both its sp. gr. and its boiling point raised by treatment with chlorosulphonic acid.

When chlorosulphonic acid is added to benzene, a violent action takes place, and torrents of hydrogen chloride are evolved.

The results obtained are sufficient to show that chlorosulphonic acid in the cold, like fuming nitric acid at a higher temperature, acts far less energetically on the normal paraffins than on the isoparaffins, the methyl derivatives of the polymethylenes or on benzene, also less energetically on the polymethylenes than on their methyl derivatives. Generally, chlorosulphonic acid acts more energetically on hydrocarbons that contain a :CH-group than on others.

There is, however, some action on the normal paraffins, and consequently there is considerable loss in the process of purification, just as there is with fuming nitric acid. In order to obtain the pure

normal paraffins from petroleum, it would be best, before subjecting them to the action of chlorosulphonic acid, to separate them more completely from other hydrocarbons by fractional distillation than was done in the case of normal heptane or normal octane.

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XXII.—Oxidation of Sulphocamphylic Acid.

By W. H. PERKIN, jun.

When sulphocamphylic acid is oxidised at 0° with potassium permanganate, the principal product is a beautifully crystalline substance which melts at 254° and, on analysis, gives numbers agreeing with the formula $C_{18}H_{22}O_7$; at 100° , it loses one molecule of water, which is probably water of crystallisation, and is converted into a substance, $C_{18}H_{20}O_{8}$, which has been named "dicampherylic acid."

Dicampherylic acid is a dibasic acid, as is shown by the analysis of its silver salt, $C_{18}H_{18}Ag_2O_6$, and of its methylic salt, $C_{18}H_{18}(CH_3)_2O_6$, its formula may, therefore, be written $C_{16}H_{18}O_2(COOH)_2$. The acid, furthermore, contains two ketonic groups, since, with hydroxylamine, it yields a dioxime, $C_{14}H_{18}(C:NOH)_2(COOH)_2$, and is, by reduction with sodium amalgam, converted into tetrahydrodicampherylic acid, $C_{14}H_{18}(CH\cdot OH)_2(COOH)_2$; its formula may, therefore, be developed to $C_{14}H_{18}(CO)_2(COOH)_2$. The most interesting property of dicampherylic acid is its decomposition by concentrated sulphuric acid at 85°, when it is converted almost quantitatively into an acid of the formula $C_9H_{10}O_8$.

$$C_{18}H_{20}O_6 = 2C_9H_{10}O_8$$
.

The determination of the nature of the acid, $C_9H_{10}O_8$, was found to be a problem of considerable difficulty, but its constitution was ultimately established by the consideration of the following facts.

This acid is a monobasic acid, giving well characterised salts, of which the silver salt, $C_9H_9AgO_8$, the beautifully crystalline methylic salt, $C_9H_9(CH_3)O_8$, and the ethylic salt, $C_9H_9(C_2H_5)O_8$, were analysed, and since, on treatment with acetic anhydride, it is converted into an acetyl compound, $C_9H_9(OC_2H_8O)O_2$, it is evident that it is a hydroxy-carboxylic acid of the composition $C_8H_8(OH)\cdot COOH$.

When exposed to the action of bromine vapour, the acid, by substitution, yields a dibromo-derivative, C₈H₆Br₂(OH) COOH, in which the bromine is so firmly united that boiling with potash does not eliminate it, a behaviour which indicates that the acid belongs to the aromatic

series. This supposition is confirmed by the fact that nitric acid converts the acid into a dinitro-derivative, $C_8H_6(NO_2)_2(OH)\cdot COOH$, an interesting substance which behaves like a dibasic acid, since its silver salt, which crystallises in dark red needles, has the formula $C_9H_6Ag_2N_2O_7$, and is evidently produced by the substitution, not only of the hydrogen of the carboxyl group, but also that of the hydroxyl group, by silver, that is, its formula may be written

C₈H₆(NO₂)₂(OAg)·COOAg.

This behaviour is quite usual in aromatic hydroxy-acids containing two nitro-groups. Thus, for example, 3:5-dinitrohydrocumaric acid, OH·C, H, (NO,), CH, CH, COOH, yields a dibasic silver salt crystallising in dark red needles, and 1:3:5-dinitroparahydroxybenzoic acid, OH·C,H,(NO,),·COOH, a dibasic salt crystallising in brown needles. From these results, it was evident that the acid CoH10O2 was either a hydroxydimethylbenzoic acid, OH·C_aH_o(CH_a)_o·COOH, or a hydroxyethylbenzoic acid, OH·C₆H₈(C₂H₅)·COOH; it could not be a hydroxyhydrocumaric acid, OH·C₆H₄·CH₂·CH₂·COOH, since the three isomeric (o-, m-, p-) forms of this acid are known, and melt respectively at 83°, 111°, and 129°, whereas the acid C₀H₁₀O₃ melts at 204°. order to determine whether it contained an ethyl group or two methyl groups, it was decided to endeavour to oxidise the acid. Before doing this, however, it was necessary to protect the hydroxyl group by converting it into a methoxy-group, and this was readily accomplished by treating the methylic salt of the acid with sodium methylate and methylic iodide in the usual way. The oily methylic salt,

OCH₃·C₈H₈·COOCH₈,

thus formed yielded, on hydrolysis, the corresponding methoxy-acid, OCH₃·C₈H₈·COOH, and this, on oxidation with permanganate, was almost quantitatively converted into an acid of the formula OCH₃·C₇H₅(COOH)₂, showing that the original acid, $C_0H_{10}O_8$, must have contained two methyl groups, one of which had been converted into COOH during the oxidation; in short, the acid $C_9H_{10}O_8$ is a dimethylhydroxybenzoic acid, OH·C₆H₂(CH₃)₂·COOH.

On heating the methoxydibasic acid, $OCH_8 \cdot C_7H_5(COOH)_2$, with hydriodic acid, the corresponding hydroxy-acid, $OH \cdot C_7H_5(COOH)_2$, was obtained as a very sparingly soluble, crystalline powder melting at 283°, and giving, in alcoholic solution, an intense reddish-violet coloration with ferric chloride. As these properties are the same as those of the hydroxymethylterephthalic acid of the formula

described by Jacobsen and H. Meyer (Ber., 1883, 16, 191), the author at first thought that the acids were identical (compare Proc., 1893, 9, 110).

The experiments up to this stage were completed in 1893, and since then, during the course of a long investigation into the properties of sulphocamphylic acid, some new facts were discovered which made it improbable that this formula could be correct.

The subject was therefore further investigated, and after much labour the relative positions in the hydroxydimethylbenzoic acid, $C_9H_{10}O_3$, and also in the hydroxymethyldicarboxylic acid, $OH \cdot C_6H_2(CH_3)(COOH)_2$, produced by its oxidation have, as the author believes, been clearly established.

In the first place, the acid, $C_9H_{10}O_8$, which melts at 204° and gives no colour with ferric chloride, is isomeric with the already known hydroxydimethylbenzoic acids, as will be seen from the following table, in which the numbers refer to the groups taken in the order $CH_3: CH_3: OH: COOH$.

```
M. p.
                                        199°
ortho-Hydroxyparaxylic acid 1:2:5:4
                                             FeCl., bluish-violet.
ortho-Hydroxymesitylenic acid 1:3:4:5
                                        179
                                              FeCl, intense blue.
para-Hydroxymesitylenic acid 1:3:2:5
                                        223
                                              FeCl, brown.
a-Hydroxyxylic acid
                                        170
                            1:3:1:4
ß-
                            1:4:2:3
                                        144
                 ,,
                            1:4:5:2
                                        153
γ
                 "
```

The careful investigation of the acid $C_9H_{10}O_8$, melting at 204°, has clearly established the following points.

- 1. The Hydroxyl Group is in the Meta-position relatively to the Carboxyl Group.—That the acid is not an orthohydroxy-acid is clearly indicated by the fact that it gives no colour with ferric chloride; that it is neither an orthohydroxy- nor a parahydroxy-acid is shown by the fact that it may be heated with concentrated hydrochloric acid or hydriodic acid at 200—220° without decomposition, whereas ortho- and parahydroxy-acids are readily decomposed into the corresponding phenols and carbonic anhydride by this treatment.
- 2. The Acid is derived from the Xylenol, $[(CH_3)_2:OH=1:2:6]$.— When the calcium salt of the acid $C_9H_{10}O_8$ is distilled with lime, it shows the behaviour characteristic of the calcium salts of metahydroxy-acids, namely, decomposition takes place with great difficulty, and only at an exceedingly high temperature. The distillate contains a xylenol, which crystallises from water in long, colourless needles, and the aqueous solution of which gives, with ferric chloride, a distinct, although not intense, bluish-violet coloration; it melts at 75° and distils constantly at 218°. The identity of this xylenol was, with difficulty, established in the following way. All the six possible

xylenols, $C_6H_3(CH_3)_2\cdot OH$, have been prepared and carefully investigated, so that their properties are well known; and in order to clearly show how the constitution of the xylenol from the acid $C_9H_{10}O_8$ was proved, a short table of the properties of the xylenols is appended, the numbers referring to the groups in the order $CH_8: CH_8: OH$.

I 1:8:5 II 1:2:6 III 1:4:2 IV 1:2:4 V 1:8:4 VI 1:8:2	b. p. 219·5° ,, 218 ,, 211·5 ,, 225 ,, 211·5 ,, 212	m. p. 68° ,, 75 ,, 75 ,, 65 ,, 26 ,, 49	FeCl ₃ , no colour. ,, violet. ,, no colour. ,, not stated. ,, blue. ,, not stated.
---------------------------------------------------------------------	-----------------------------------------------------	-----------------------------------------	------------------------------------------------------------------------------------------------

Three of these xylenols, namely, Nos. III, IV, and V, were obtained from Schuchardt, and after very careful purification found to be different from the author's xylenol, as, indeed, the melting and boiling points would indicate. Since, again, both the melting point and boiling point of No. VI differ markedly from those of the author's xylenol, there remain only Nos. I and II as possibly representing its constitution, and of these, No. II is the more probable, since this melts and boils at exactly the same temperatures, whereas No. I has a lower melting point, and is stated to give no coloration with ferric chloride. As, however, very slight traces of impurity considerably depress the melting point of the xylenols, and as the colour with ferric chloride is not pronounced in the case of any one of them, it was necessary to obtain further evidence before deciding this question of identity. Fortunately, there is a wide difference in the melting points of the tribromo-xylenols derived from Nos. I and II, that from the former melting at 166°, whereas that from the latter melts at 184°, and on trying the experiment with the author's xylenol it was found that its tribromo-derivative melted sharply at 184°; there can, therefore, be no doubt that the constitution of this xylenol is represented by the formula $C_6H_8(CH_8)_2 \cdot OH = 1:2:6$.

Since, then, the acid, $OH \cdot C_6H_2(CH_3)_2 \cdot COOH$, from which this xylenol was obtained is a metahydroxy-acid, it can only have the formula $C_6H_2(CH_8)_2(COOH) \cdot OH = 1:2:4:6$; that is, it is metahydroxyparaxylic acid, and closely allied to orthohydroxyparaxylic acid, [1:2:4:5], which Reuter (Ber., 1878, 11, 30) prepared by fusing pseudocumenesulphonic acid with caustic potash (compare Jacobsen, Ber., 1899, 12, 436). This is the second occasion on which a derivative of pseudocumene has been obtained indirectly from sulphocamphylic acid, as Koenigs and Meyer (Ber., 1894, 27, 3468, compare Trans., 1898, p. 840) found previously that isolauronic acid was readily converted into paraxylic acid by the action of sulphuric acid.

The hydroxy-dibasic acid, produced indirectly by the oxidation of

metahydroxyparaxylic acid as described above, is evidently an orthohydroxy-acid, since its alcoholic solution gives an intense blue coloration with ferric chloride; it can, therefore, only be a hydroxymethylterephthalic acid of the formula

 $OH \cdot C_6H_9(CH_8) \cdot COOH_9$ [$CH_8 \cdot COOH : OH : COOH = 1 : 3 : 5 : 6$],

and the difference between this formula and that originally assigned to this acid (see p. 176) is simply in the position of the hydroxyl group.

Unfortunately, like so many other instances in which benzene compounds have been obtained from camphor and its derivatives, the formation of metahydroxyparaxylic acid throws very little light on the constitution of dicampherylic acid, from which it is so readily produced, and although it would be easy to suggest a formula for the latter acid, the author prefers not to do so until further experimental data are forthcoming.

With regard to the formation of such benzene derivatives as xylene, cymene, pseudocumene, carvacrol, acetylortho-xylene, and others from camphor, and of derivatives of paratoluic acid and paraxylic acid from camphoric acid, the author entirely shares the opinion, somewhat differently expressed by Aschan, ammely, that until we understand the extraordinary mechanism of the production of these benzene derivatives, their formation is of little value in determining the constitution of the substances from which they are derived.

The author is much indebted to Messrs. B. Prentice, J. L. Heinke, F. H. Lees, and others for their valuable assistance in the experimental part of this investigation.

The author also wishes to state that the heavy cost of the very large amount of material used in this research was to a very considerable extent covered by repeated large grants from the Government Grant Fund of the Royal Society.

EXPERIMENTAL.

Oxidation of Sulphocamphylic Acid. Formation of Dicampherylic Acid, $C_{18}H_{20}O_6+H_2O.$

In carrying out this oxidation, sulphocamphylic acid in quantities of 50 grams was dissolved in about 1 litre of water, the solution neutralised with potassium carbonate, and transferred to a flat porcelain basin in which a turbine was fitted. The solution was cooled to 0° by adding powdered ice, and a cold saturated solution

Structur und stereochemische Studien in der Camphergruppe; Helsingfors, 1895, p. 17.

of potassium permanganate run in slowly until the colour, which instantly disappears at first, just remained permanent, care being taken that the whole was well stirred and the temperature kept below 2° during the operation. The product from several such oxidations was filtered, the filtrate and washings of the manganese precipitate evaporated to a small bulk, and the concentrated yellow solution acidified and allowed to stand overnight; the yellow, crystalline precipitate which had separated was collected, washed with water, and purified by repeated crystallisation from dilute acetic acid; the magnificent, lemon-yellow prisms thus obtained, after standing for some days on a porous tile in contact with air, gave the following results on analysis.

These crystals, when heated for a long time at 100° , gradually lose water, a change which takes place rapidly at $120-130^\circ$. $1\cdot0952$ grams of the substance, dried in the air, lost $0\cdot0610$ gram at 100° , or $5\cdot47$ per cent., whereas the calculated loss, supposing $C_{18}H_{22}O_7$ to be converted into $C_{18}H_{20}O_6$ at 100° , is $5\cdot14$ per cent. An analysis of the substance, dried at 120° until of constant weight, gave the following result.

0.1496 gave 0.3571 CO₂ and 0.0851 H₂O.
$$C = 65.10$$
; $H = 6.32$. $C_{18}H_{20}O_6$ requires $C = 65.06$; $H = 6.02$ per cent.

The molecular weight of this substance was determined by the cryoscopic method, when it was found that 0.8010 gram, dissolved in 36.1 grams of acetic acid, depressed the melting point 0.26°, this corresponding with a molecular weight 332, whereas the molecular weight of $\rm C_{18}H_{20}O_6$ is 332 and of $\rm C_{18}H_{22}O_7$ 350.

On long standing in an uncorked flask, the solution used in this determination deposited a mass of slender, colourless needles which looked like threads of asbestos and quite unlike the hard prisms in which the substance $C_{18}H_{22}O_7$ usually crystallises. An analysis showed, however, that the crystals had the composition $C_{18}H_{22}O_7$.

0.1028 gave 0.2328 CO₂ and 0.06 H₂O.
$$C = 61.76$$
; $H = 6.48$. $C_{18}H_{22}O_7$ requires $C = 61.71$; $H = 6.28$ per cent.

These results, taken together with those described in the following pages, show that the product of the oxidation of sulphocamphylic acid is a substance of the formula $C_{18}H_{20}O_6$, which crystallises with water in prisms of the composition $C_{18}H_{22}O_7$.

This compound, which has been named dicampherylic acid, melts at about 254°, and is readily soluble in alcohol, acetone, acetic acid, and ethylic acetate, but only very sparingly in benzene; it is almost insoluble in cold water, although, in a finely divided state, it dissolves appreciably in boiling water, and separates on cooling in almost colourless, prismatic crystals. It dissolves readily in dilute sodium carbonate, and, although the well-cooled solution does not decolorise permanganate, it does so readily on warming.

Dicampherylic acid dissolves readily in warm, concentrated nitric acid, and, on boiling, oxidation takes place so slowly that even after 10 minutes the addition of water causes a large quantity of the substance to separate unchanged. Fuming hydriodic acid dissolves the finely-powdered crystals easily, and if, after boiling for a short time, the bulk of the hydriodic acid is distilled off, the residue, on mixing with water, deposits a heavy, dark brown oil which becomes colourless on the addition of sulphurous acid and smells like isoamylic iodide.

Salts of Dicampherylic Acid.

That this acid is a dibasic acid was first shown by titrating a weighed quantity of the anhydrous crystals with standard alkali, when it was found that 0.4416 required for neutralisation 0.1495 gram KOH, or 33.8 per cent., whereas a dibasic acid of the formula $C_{18}H_{20}O_6$ requires 33.7 per cent.

The silver salt was obtained as a white, gelatinous precipitate on adding silver nitrate to a warm, neutral solution of the ammonium salt, the precipitate on warming with much water for about an hour becomes crystalline, and is then readily filtered and washed. The analyses seem to show that this salt, after drying over sulphuric acid in a desiccator, has the formula $C_{18}H_{20}Ag_2O_7$, and that at $120-130^\circ$ it loses water, and then has the formula $C_{18}H_{18}Ag_0O_6$.

The silver salt, dried over sulphuric acid in a desiccator, gave the following results on analysis.

0.2054 gave 0.2833 CO_{2} , 0.0696 $H_{2}O$, and 0.0790 Ag. C = 37.66; H = 3.77; Ag = 38.46.

0.2469 gave 0.3420 CO_2 , 0.0746 H_2O , and 0.0953 Ag. C = 37.77; H = 3.36; Ag = 38.58.

0.3390 gave, on ignition, 0.1302 Ag. Ag = 38.41.

 $C_{18}H_{20}Ag_2O_7$ requires C = 38.29. H = 3.55; Ag = 38.29 per cent.

This salt may be heated at 120—130° without decomposition, and after its weight had become constant it was analysed.

0.2260 gave 0.3223 CO_2 , 0.0681 H_2O , and 0.0887 Ag. C = 38.89; H = 3.35; Ag = 39.24.

0.22, on ignition, gave 0.0860 Ag. Ag = 39.09.

 $C_{18}H_{18}Ag_2O_6$ requires C = 39.56; H = 3.30; Ag = 39.56 per cent.

A neutral solution of the ammonium salt of dicampherylic acid gives a heavy, white precipitate with lead acetate, but no precipitate with barium, calcium, or zinc chlorides; copper acetate gives no precipitate in the cold, but on boiling a light blue, crystalline, copper salt separates.

Methylic Dicampherylate, $C_{18}H_{18}(CH_8)_2O_6$.—This salt was prepared by two different methods.

- 1. The dry silver salt of the acid was digested for 2 hours with ether and excess of methylic iodide, and the ethereal solution filtered; the residue was extracted repeatedly with ether, and the combined ethereal solutions evaporated to a small bulk. On standing, beautiful crystals separated which, after crystallisation from benzene, melted at $226-227^{\circ}$.
- 2. The acid, dissolved in methylic alcohol, was mixed with concentrated sulphuric acid and heated to boiling on a water-bath for a few minutes; on cooling, glistening crystals separated, which, after collecting, and recrystallising from benzene, melted at 226—227°. This substance, which, like all the derivatives of dicampherylic acid, is very difficult to burn, was analysed, with the following results.
 - I. 0.1692 gave 0.4120 CO₂ and 0.1040 H₂O. C = 66.42; H = 6.83.
 - II. 0.1652 , 0.4011 CO_2 , 0.0996 H_2O . C = 66.22; H = 6.69.
 - III. 0·1663 ,, 0·4027 CO_2 ,, 0·1007 H_2O . C = 66·04; H = 6·73. $C_{18}H_{18}(CH_8)_{2}O_6$ requires C = 66·66; H = 6·66 per cent.

In No. I, the methylic salt used was prepared from the silver salt, and in Nos. II and III from the acid by treatment with methylic alcohol and sulphuric acid.

Action of Hydroxylamine on Dicampherylic Acid.

In studying the action of hydroxylamine on dicampherylic acid, the pure acid (2 grams), dissolved in dilute potash (6 grams), was mixed with hydroxylamine hydrochloride (2 grams), and acidified after 12 hours, when the nearly pure oxime separated in white flocks.* The whole was extracted with much ether, the ethereal solution rapidly† dried

- * In this form, the oxime is readily soluble in ether, and also in warm water, but after crystallisation from ether, it becomes almost insoluble, both in this solvent and in water.
- † If this operation is not very quickly performed, the oxime is apt to separate on the lumps of calcium chloride.

with calcium chloride, filtered, and allowed to stand either as it was, or, better, after concentrating somewhat, when the oxime separated in crystalline crusts. These crusts, after washing with ether, gave the following results on analysis.

I. 0.1420 gave 0.3090 CO₂ and 0.0830 H₂O. C=59.35; H=6.50. II. 0.1548 , 0.3362 CO₂ , 0.0914 H₂O. C=59.23; H=6.57. III. 0.1699 , 0.3663 CO₂ , 0.0986 H₂O. C=58.80; H=6.44. IV. 0.1608 , 0.3487 CO₂ , 0.0937 H₂O. C=59.14; H=6.47. V. 0.2602 , 17.4 c.c. nitrogen at 18° and 758 mm. N=7.70. Other nitrogen determinations gave N=6.90, 7.30, and 7.05.

 $C_{18}H_{22}N_2O_6$ requires C = 59.66; H = 6.07; N = 7.73 per cent.

This substance is, therefore, the dioxime of dicampherylic acid produced according to the equation

 $C_{18}H_{20}O_6 + 2NH_2 \cdot OH = C_{18}H_{20}O_4(N \cdot OH)_2 + 2H_2O.$

When heated in a capillary tube, the oxime turns brown at 210—220°, and gradually becomes darker as the temperature rises, but does not melt completely at 250°. It is almost insoluble in ether and most organic solvents, but dissolves in concentrated hydrochloric acid, and is reprecipitated unchanged when the solution is diluted with water and warmed; it dissolves also in caustic potash solution, and is reprecipitated unchanged by hydrochloric acid.

Action of Acetic Anhydride on the Dioxime.—The pure dioxime dissolves slowly, but completely in cold acetic anhydride, and if the solution is allowed to remain in contact with air, a crystalline cake gradually forms; this, after recrystallisation from dilute acetic acid, gave the following results on analysis.

This substance, which is doubtless the acetate of the dioxime, $C_{18}H_{22}N_2O_6$, $C_2H_4O_9$, melts at 184°, and crystallises from dilute acetic acid in microscopic needles; when heated at 190—200°, it froths up and emits an odour of acetic anhydride. Dilute potash hydrolyses this acetate, and on acidifying and extracting with ether in the usual way, the characteristic crusts of the regenerated dioxime are obtained.

0.3153 gave 22.5 c.c. nitrogen at 22° and 758 mm. N = 8.06. $C_{18}H_{22}N_{2}O_{5}$ requires N = 7.73 per cent.

Action of Phenylhydrazine on Dicampherylic Acid.

When dicampherylic acid (3.5 grams) is mixed with freshly-distilled phenylhydrazine (5 grams) and glacial acetic acid (10 grams), and the mixture heated on the water-bath, reaction sets in in a short time with evolution of gas, the liquid soon becomes dark-red, and after 20 minutes crystals begin to separate. As soon as the separation appears to be complete, the whole is filtered hot on a platinum cone,* and the crystals washed with acetic acid and recrystallised from this solvent. The ruby-red crystals thus obtained are very difficult to burn, and for this reason several analyses were made, with the following results.

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0·1487 gave 0·3736 CO<sub>2</sub> and 0·0820 H<sub>2</sub>O. C=68·50; H=6·13. 0·1735 ,, 0·4333 CO<sub>2</sub> ,, 0·0957 H<sub>2</sub>O. C=68·16; H=6·13. 0·1562 ,, 0·3873 CO<sub>2</sub> ,, 0·0908 H<sub>2</sub>O. C=67·62; H=6·46. 0·1963 ,, 18·5 c.c. nitrogen at 21° and 753 mm. N=10·64.
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These analytical numbers agree best with the formula $C_{30}H_{84}N_4O_5$, which would be obtained by the combination of 1 mol. of dicampherylic acid and 2 mols. of phenylhydrazine with loss of water, $C_{18}H_{20}O_6 + 2C_6H_5\cdot NH\cdot NH_2 = C_{80}H_{34}N_4O_5 + H_2O$, or it is possible that it is the dihydrazone of $C_{18}H_{20}O_6$ crystrallising with $1H_2O$.

This substance dissolves in hot acetic acid or alcohol, forming yellow solutions which, on cooling, deposit brilliant, ruby-red crystals. When heated in a capillary tube, it darkens at 230°, and decomposes with evolution of gas and charring at 237°. It dissolves in alkalis and alkali carbonates, forming yellow solutions, which, on acidifying, give a bright yellow precipitate, consisting, apparently, of the unchanged substance.

Reduction of Dicampherylic Acid. Formation of Tetrahydrodicampherylic Acid, $C_{18}H_{24}O_{6}$.

In order to investigate this reduction, pure dicampherylic acid was dissolved in dilute soda and treated in a flat basin with a large excess of sodium amalgam (5 per cent.), and after 24 hours, the whole was neutralised, filtered, and the filtrate acidified and extracted many times with ether. The ethereal solution, after drying and concentrating, deposited the greater part of the product of reduction in crystalline flakes. These were collected, washed with ether, and analysed.

^{*} The mother liquors when heated with more phenylhydrazine give another crop of crystals.

The determination of the molecular weight of this acid by the boiling point method, using alcohol as the solvent, gave 298, 307, and 296, whereas the calculated molecular weight for $C_{18}H_{24}O_{6}$ is 336.

Tetrahydrodicampherylic acid melts at about 297—298° with evolution of gas. It is sparingly soluble in methylic and ethylic alcohols and acetic acid in the cold, and in boiling water, and is not readily soluble even in boiling acetic acid; but from its solution in dilute acetic acid it separates, on long standing, in four-sided plates.

Silver Tetrahydrodicampherylate.—When a hot, dilute solution of the ammonium salt of the acid is mixed with silver nitrate, a white precipitate is formed, and if this be rapidly removed with the aid of the pump, the filtrate, on standing, deposits beautiful groups of colourless crystals of a silver salt; this, on analysis, gave the following numbers.

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0.2169 gave 0.3070 CO_2, 0.0826 H_2O, and 0.0846 Ag. C=38.60; H=4.18; Ag=39.0. C_{18}H_{22}Ag_2O_6 requires C=39.27; H=4.0; Ag=39.27 per cent.
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Fusion of Dicampherylic Acid with Potash.

Fifteen grams of the pure acid was mixed with 50 grams of potash and a little water, and heated at about 120°, when the crystals rapidly dissolved, forming a dark solution, which readily crystallised owing to the separation of a potassium salt. On raising the temperature, the liquid became dark brown, and then red, and after much frothing suddenly solidified at about 165°, a peculiar aromatic smell being noticeable; more potash (20 grams) was then added, and the temperature gradually raised, until, at 250°, the frothing had entirely ceased. The melt was dissolved in water, acidified, and extracted 10 times with ether, the ethereal solution evaporated, and the viscid residue, which smelt strongly of fatty acids, distilled in a current of steam. The strongly acid distillate, when neutralised with pure calcium carbonate and concentrated, deposited beautiful, feathery crystals of calcium isobutyrate; these were collected and analysed.

Determination of Water of Crystallisation. -0.2426 gram, on heating at 100° until constant, lost 0.0674 gram $H_2O = 27.79$.

 $(C_4H_7O_2)_2Ca + 5H_2O$ requires $H_2O = 29.60$ per cent.

^{*} Compare Crossley and Perkin, Trans., 1898, 73, 15.

0.1752 gave 0.1107 CaSO₄. Ca = 18.58. $(C_8H_7\cdot COO)_2$ Ca requires Ca = 18.67 per cent.

The remainder of the calcium salt was dissolved in water, acidified with hydrochloric acid, and the oily acid which separated extracted with ether; the dried ethereal solution, after the ether had been removed on the water-bath, left an oily residue of isobutyric acid which distilled at 154—155°.

0.1684 gave 0.3347 CO₂ and 0.1368 H_2O . C = 54.21; H = 9.08. C_8H_7COOH requires C = 54.54; H = 9.09 per cent.

This acid, which is undoubtedly isobutyric acid, is formed in considerable quantities during this fusion, as the amount obtained from 15 grams of dicampherylic acid could hardly have been less than 3 grams.

The residue in the distilling flask, after the isobutyric acid had been removed by steam, contained a flocculent precipitate; this was removed by filtration, and the filtrate extracted five times with ether. The ethereal solution, on evaporation, deposited 9 grams of an almost colourless, thick, oily acid, which showed no signs of crystallising, even after standing for some weeks over sulphuric acid. On analysis, it gave the following numbers.

0.1535 gave 0.3364 CO₂ and 0.0842 H₂O. C=59.77; H=6.11. $C_9H_{10}O_4$ requires C=59.34; H=5.50 per cent.

In the hope of obtaining this acid in a crystalline condition, it was converted into its lead salt, by adding lead acetate to its aqueous solution, and the white precipitate, which looked almost crystalline, was suspended in water and decomposed by hydrogen sulphide; the filtrate, after concentration, was extracted with pure ether, &c., in the usual way, and the residue, on being allowed to remain over sulphuric acid in a vacuum desiccator, left a colourless, syrupy acid which, on analysis, gave the following results.

The silver salt, which was obtained as a white, amorphous precipitate on adding silver nitrate to a neutral solution of the ammonium salt, gave the following results on analysis.

0.2157 gave 0.2184 CO₂, 0.0469 H₂O, and 0.1173 Ag. C = 27.61; H = 2.41; Ag = 54.38.

 $C_9H_8Ag_2O_4$ requires $C=27\cdot 28$; $H=2\cdot 02$; $Ag=54\cdot 54$ per cent.

This acid, which appears to have the formula C7H8(COOH)2, is very

readily soluble in water; when heated, it gives a yellow distillate which is insoluble in cold water, but dissolves on boiling, and therefore very probably consists of the anhydride. The solution of the acid in sodium carbonate does not decolorise permanganate at ordinary temperatures except on long standing.

It should be mentioned that, in one experiment on the fusion of dicampherylic acid with potash, a small quantity of an acid was obtained which was almost insoluble in water, and only very sparingly soluble in boiling glacial acetic acid. This acid, which crystallised from acetic acid in needles and melted above 300°, was at first thought to be terephthalic acid, but this is not the case, since its methylic salt is a syrup.

Metahydroxyparaxylic Acid, $C_6H_2(CH_3)_2(COOH)$ ·OH [=1:2:4:6].

This acid, as stated in the introduction, is formed by the action of concentrated sulphuric acid at 85° on dicampherylic acid. The finely-divided acid dissolves readily in warm, concentrated sulphuric acid, forming a yellow solution which, if heated at 80—85°, gradually becomes darker, the decomposition of the dicampherylic acid being complete in about 10 minutes. On pouring the product into water, an ochreous precipitate separates which is collected on the pump, washed well with water, dissolved in dilute sodium carbonate, boiled with animal charcoal, filtered, and the acid reprecipitated. The now almost colourless acid is further purified by recrystallisation, first from glacial acetic acid, and then from water.

Metahydroxyparaxylic acid melts at 203—204°, and when strongly heated, as, for example, during the combustion, a portion chars, but the main quantity sublimes in beautiful, colourless crystals. It is readily soluble in alcohol and ether, moderately so in hot water and in glacial acetic acid, but only sparingly in chloroform, light petroleum, benzene, carbon bisulphide, and cold water; its aqueous solution gives no coloration with ferric chloride. From glacial acetic acid, it crystallises beautifully in nearly colourless, glistening plates, which, on exposure to the air, become opaque and chalky, a change which takes place rapidly at 100°; from water, the acid also crystallises well. Hydroxyparaxylic acid does not react with hydroxylamine, and is not reduced by sodium amalgam at the ordinary temperature, or when its solution in hydriodic acid is boiled for some time; at 200—220°, however,

fuming hydriodic acid and phosphorus slowly attack it, with formation of a small quantity of a neutral substance of phenolic nature, but even at this temperature most of the acid remains undecomposed. The great stability of the acid is furthermore clearly shown from the following experiment.

1.5 grams of the pure acid was heated with 10 c.c. of concentrated hydrochloric acid at 230—235° for 8 hours; the tube contained a good deal of charcoal, and the greenish liquid, which had a phenolic odour, was filled with long, silky needles like asbestos threads; these crystals were collected and purified by dissolving in potash, filtering, and reprecipitating with hydrochloric acid; the substance then melted at 202°, and consisted of unchanged hydroxyparaxylic acid, as the following analysis shows.

0.1395 gave 0.3320 CO₂ and 0.0778 H₂O. C = 64.92; H = 6.19. $C_9H_{10}O_3$ requires C = 65.06; H = 6.03 per cent.

The amount of acid recovered in this experiment was 1.1 grams.

Salts of Hydroxyparaxylic Acid.

The silver salt, $C_9H_9AgO_3$, was obtained, on adding silver nitrate to a neutral solution of the ammonium salt, as a white, amorphous precipitate. It decomposes readily on heating, yielding a beautifully crystalline sublimate. The following results were obtained on analysis.

0·1736 gave 0·2486 CO₂, 0·0548 H₂O, and 0·0680 Ag. C = 39·05; H = 3·51; Ag = 39·18.

0.1562 gave 0.0617 Ag. Ag = 39.50. $C_0H_0AgO_3$ requires C = 39.56; H = 3.30; Ag = 39.56.

The neutral solution of the ammonium salt of hydroxyparaxylic acid gives no precipitate with calcium* or barium chlorides.

Methylic Hydroxyparaxylate, OH·C₆H₂(CH₈)₂·COOCH₈.—In order to prepare this salt, the acid (22 grams), dissolved in methylic alcohol (150 c.c.), was mixed with concentrated sulphuric acid (40 c.c.) and heated to boiling for half an hour; more sulphuric acid (10 c.c.) was then added, the boiling continued for half an hour, and the whole allowed to stand overnight. The beautiful, striated, leaf-like crystals which separated were collected with the aid of the pump, and, after washing with water and drying at 100°, were found to weigh 13·8 grams. The brown mother liquors, on diluting with water, deposited a brown oil which, on shaking and stirring, slowly solidified; this crude product, after washing and drying on a porous plate at 100°,

^{*} For a description of the calcium salt of hydroxyparaxylic acid, see p. 192.

weighed 7.5 grams. Each portion was separately crystallised from benzene, and in this way 17 grams of the pure methylic salt was obtained, showing that the acid is easy to etherify.

Methylic hydroxyparaxylate melts at 148—149°, and in its other properties closely resembles the corresponding ethylic salt.

Ethylic hydroxyparaxylats, OH·C₆H₂(CH₈)₂·COOC₂H₅.—This was prepared by treating the acid with ethylic alcohol and sulphuric acid in the same way as the methylic salt.

The colourless needles obtained by crystallisation from light petroleum melted at 134—135°, and gave the following results on analysis.

Ethylic hydroxyparaxylate is readily soluble in alcohol and benzene, but rather sparingly in light petroleum; its solution in alcohol gives no coloration with ferric chloride.

It is insoluble in sodium carbonate, but dissolves readily in caustic potash solution, and is reprecipitated unchanged on the addition of acid. When heated in small quantities, it distils unchanged.

In order to prepare this substance, hydroxyparaxylic acid (1 gram) was boiled with acetic anhydride (10 grams) in a reflux apparatus for half an hour, and the product, when cold, was shaken with water until the excess of anhydride had been removed.

The acetyl compound, which separated as a crystalline cake, was purified by recrystallisation, first from methylic alcohol and then from benzene.

Acetoxyparaxylic acid crystallises in colourless, stellate groups, melts at 141—142°, and when rapidly heated in small quantities it distils with only very slight decomposition. It is readily soluble in benzene, alcohol, and ethylic acetate, but almost insoluble in light petroleum; it dissolves with difficulty in, and is only very slowly hydrolysed by,

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boiling water, but is readily decomposed by boiling with potassium carbonate solution, and, on acidifying, pure hydroxyparaxylic acid separates.

$$\begin{array}{c} \text{CH}_8 \\ \text{Dinitrohydroxyparaxylic Acid, } \begin{array}{c} \text{OH} \\ \text{NO}_2 \end{array} \\ \\ \text{COOH} \end{array}$$

When pure hydroxyparaxylic acid is added, in small quantities at a time, to strong nitric acid, it hardly dissolves, and no change takes place until the mixture is gently warmed, when suddenly a vigorous action sets in, the substance passes into solution, and each fresh quantity added dissolves with a slight hissing sound and abundant evolution of red fumes. In a short time, beautiful, yellow crystals separate, and after cooling and mixing with an equal bulk of water, further precipitation takes place. The yellow crystals were collected, washed with water, recrystallised from this solvent and analysed, with the following results.

0.1818 gave 0.2838 CO₂ and 0.0562 H₂O. C=42.57; H=3.43. 0.1637 , 0.2535 CO₂ , 0.0496 H₂O. C=42.23; H=3.36.

0.1996 , 19.2 c.c. nitrogen at 22° and 754 mm. N = 10.81.

 $OH \cdot C_6(CH_8)_2(NO_2)_2 \cdot COOH$ requires $C = 42 \cdot 19$; $H = 3 \cdot 12$; $N = 10 \cdot 94$ per cent.

Dinitrohydroxyparaxylic acid is readily soluble in alcohol, acetone, ethylic acetate, and acetic acid, moderately so in hot water, but only sparingly in cold water, benzene, and chloroform. It crystallises from water in glistening, yellow plates, and dissolves in dilute sodium carbonate, forming a deep orange solution. When heated in a capillary tube, it darkens at 195°, and decomposes rapidly at 203—205° with evolution of gas.

Salts of Dinitrohydroxyparaxylic Acid.

The Silver Salt, OAg·C₆(CH₃)₂(NO₂)₂·COOAg.—When silver nitrate is added to a moderately concentrated and slightly alkaline solution of the ammonium salt of the acid, no precipitate is produced at first, but, on standing, a splendid, dark purple, crystalline silver salt separates, which, under the microscope, is seen to consist of fern-like groups of needles. As this salt appeared to be explosive, the silver was determined by heating the substance with nitric acid and hydrochloric acid in a sealed tube at 180° and weighing the silver chloride formed.

0.1466 gave 0.0892 AgCl. Ag = 45.70. $C_0H_6Ag_2N_2O_7$ requires Ag = 45.95 per cent. This analysis shows that, in the formation of this salt, the hydrogen of the hydroxyl group, as well as that of the carboxyl group, has been replaced by silver (see p. 176). This silver salt is moderately easily soluble in warm water, and may be recrystallised from this solvent, but, apparently, with a good deal of decomposition.

The faintly alkaline, dilute, orange-coloured solution of the ammonium salt of dinitrohydroxyparaxylic acid gives no precipitate with copper acetate, barium chloride, or zinc acetate, but lead acetate produces a very sparingly soluble, heavy, yellow precipitate, and ferric chloride a brownish-red precipitate.

The action of bromine on hydroxyparaxylic acid was investigated in the following way: 3.9608 grams of the pure, finely powdered acid was exposed in a glass dish to the action of bromine vapour for 12 hours, during which time much hydrogen bromide was produced; after removing the excess of bromine by exposure over solid potash in a vacuum desiccator, it was found that 3.6932 grams of bromine had been absorbed. Representing the reaction by the equation,

$$C_0H_{10}O_8 + 2Br_2 = C_0H_8Br_2O_8 + 2HBr_2$$

the increase in weight should have been 3.769 grams.

A determination of the bromine in this crude substance gave the following result.

0.2378 gram gave 0.2698 AgBr. Br = 48.27. $C_9H_8Br_2O_8$ requires Br = 49.38 per cent.

It is difficult to crystallise the crude substance, and the only way this could be accomplished was to dissolve it in a little methylic alcohol, add a good deal of chloroform, and evaporate to a small bulk to remove most of the methylic alcohol; if, now, more chloroform is added and, after rapidly concentrating, the liquid is allowed to stand, the supersaturated solution rapidly deposits well-shaped, prismatic crystals, which, on analysis, gave the following results.

0.1836 gave 0.2246 CO₂ and 0.0428 H₂O. C = 33.37; H = 2.58. 0.3218 , 0.3726 AgBr. Br = 49.25.

 $C_9H_8Br_2O_8$ requires C = 33.33; H = 2.47; Br = 49.38 per cent.

Dibromhydroxyparaxylic acid melts at 204—205°, and is very readily soluble in alcohol, but only sparingly in chloroform; when pure, it crystallises well from dilute alcohol.

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It is a very stable substance, and may be boiled for some time with caustic potash without decomposing.

A determination of the molecular weight of this bromo-acid by Raoult's method, using acetic acid as the solvent, gave M = 333, whereas the value calculated from the formula $C_0H_8Br_2O_8$ is 324.

$$1:2\text{-}\boldsymbol{Xylenol(6)}\quad \text{OH} \qquad \begin{array}{c} \text{CH}_8\\ \text{CH}_8 \end{array}$$

This xylenol is produced, as explained in the introduction, when the calcium salt of hydroxyparaxylic acid is distilled with lime.

The calcium salt was prepared by boiling finely divided hydroxy-paraxylic acid (30 grams) with water and a slight excess of pure calcium carbonate, filtering, and evaporating nearly to dryness, when, on standing, the calcium salt separated in warty masses.

The dried salt was finely powdered, mixed intimately with slaked lime (50 grams), and distilled in small quantities from small retorts over a blow-pipe, as great heat is necessary to bring about the de-The distillate, which was an aqueous liquid containing composition. dark-coloured, semi-solid masses and smelling very strongly of phenol, was mixed with a slight excess of caustic soda, decolorised by boiling with animal charcoal, filtered, and the filtrate acidified with hydro-The oily precipitate solidified rapidly and almost comchloric acid. pletely, and after collecting, washing, and spreading on a porous plate, an almost colourless, crystalline mass (3 grams) was obtained. submitting this to distillation, nearly the whole passed over at 218° (760 mm.) as a colourless oil which, on cooling, at once solidified. The distillate, dissolved in a considerable quantity of water at 70°, on slowly cooling, deposited very long, colourless needles, which were dried, first on a porous plate and then at 60°, and analysed.

0.1415 gave 0.4075 CO₂ and 0.1053 H₂O. C = 78.54; H = 8.27. $C_6H_8(CH_8)_2$.OH requires C = 78.69; H = 8.19 per cent.

This substance, which has been found to be 1:2-xylenol(6), melts at 74-75°, and is moderately soluble in hot water; its cold, saturated, aqueous solution gives a distinct, although not intense, bluish-violet coloration with ferric chloride, and, on standing, the solution rapidly becomes opaque (compare Töhl, Ber., 1885, 18, 2562; Nölting and Forel, ibid., p. 2673).

Tribromo-xylenol, C₆Br₈(CH₈)₂·OH.—This substance, which has already been described by Töhl (loc. cit.), was prepared by adding about 0.5 gram of the xylenol obtained in the above experiment, in small

quantities at a time, to 3 grams of bromine, care being taken to moderate the vigorous reaction by cooling; after 2 hours, the product was poured on to a glass dish, and left over potash in a desiccator until the excess of bromine had been removed, the residue being purified by recrystallisation from the dilute alcohol.

0.2840 gave 0.4440 AgBr. Br. = 66.52. $C_gH_7Br_gO$ requires Br = 66.85 per cent.

This tribromo-xylenol crystallises from dilute alcohol in long, pale-yellow needles which melt at 184°, and it thus agrees in its properties with the tribromo-derivative which Töhl obtained by brominating 1:2-xylenol (6).

Methoxyparaxylic Acid, $[(CH_3)_2 : COOH : OCH_8 = 1 : 2 : 4 : 6]$.

With the object of obtaining further information as to the constitution of the acid CoH10Os, now known to be hydroxyparaxylic acid, it was decided to endeavour to oxidise one or more methyl groups, and in order to do this it was necessary, in the first instance, to protect the hydroxyl group in the usual way, namely, by substituting methyl or ethyl for hydrogen. For this purpose, in the first experiments, the methylic salt of the acid (15 grams) was mixed with a solution of sodium (2 grams) in methylic alcohol and methylic iodide (25 grams), and the mixture heated first at 95-110° for 2 hours, and afterwards at 120—130° for 2 hours. The light-brown product was evaporated on the water-bath, water added, and the heavy oil extracted with ether; the ethereal solution, on evaporation, deposited an oil which did not show any signs of crystallising, and which, doubtless, consisted of the methylic salt of methoxyparaxylic acid, $OCH_3 \cdot C_6H_2(CH_3)_2 \cdot COOCH_3$. This was not analysed, but at once hydrolysed by boiling with excess of methyl alcoholic potash for 2 hours; after evaporating the methylic alcohol, and acidifying the aqueous solution of the residue, a very bulky, white precipitate was obtained, which was purified by recrystallisation from 50 per cent. alcohol.

0.1375 gave 0.3356 CO₂ and 0.0823 H₂O. C=66.56; H=6.64. C₆H₂(CH₃)₂(OCH₃).COOH requires C=66.66; H=6.66 per cent.

Methoxyparaxylic acid melts at 170—171°, and distils at a high temperature, apparently without decomposition. It is very sparingly soluble in hot water, and almost insoluble in cold water; it crystallises from boiling water in woolly masses consisting of fine needles. It is readily soluble in acetic acid, methylic alcohol, chloroform, and ethylic acetate, but only sparingly in carbon bisulphide and light petroleum; it crystallises splendidly from ethylic acetate in long, colourless prisms.

Ethylic Ethoxyparaxylate, $OC_2H_5 \cdot C_6H_2(CH_3)_2 \cdot COOC_2H_5$.

This was prepared by heating ethylic hydroxyparaxylate (2 grams) with sodium (0.26 gram) dissolved in alcohol, and ethylic iodide (5 grams) at 120—130° for 2 hours, evaporating the product on the water-bath, and adding water, when an oil separated which rapidly solidified. The crystalline mass was collected, washed with water, left in contact with porous porcelain until free from oil, and recrystallised from dilute methylic alcohol, when glistening prisms were obtained which gave the following results on analysis.

0.1496 gave 0.3841 CO₂ and 0.1110 H₂O.
$$C = 70.02$$
; $H = 8.24$. $C_{18}H_{18}O_{8}$ requires $C = 70.27$; $H = 8.11$ per cent.

Ethylic ethoxyparaxylate melts at 50—51°, and is readily soluble in methylic alcohol, light petroleum, benzene, chloroform, and carbon bisulphide.

$$\textbf{\textit{Ethoxyparaxylic Acid}, OC}_2\textbf{H}_5\textbf{\cdot}\textbf{C}_6\textbf{H}_2(\textbf{CH}_8)_2\textbf{\cdot}\textbf{COOH}.$$

When boiled with alcoholic potash, ethylic ethoxyparaxylate is readily hydrolysed, and if the product is mixed with water and evaporated until free from alcohol, the addition of hydrochloric acid to the cold aqueous solution precipitates the acid as a white powder which crystallises from methylic alcohol in beautiful, glistening, prismatic needles.

Ethoxyparaxylic acid melts at 173—174°; it is sparingly soluble in water and light petroleum, but readily in ethylic and methylic alcohols, benzene, and ethylic acetate.

Methoxyparaxylic acid is moderately readily acted on by potassium permanganate in alkaline solution, with formation, in the first instance, of methoxymethylterephthalic acid. In studying this oxidation, the pure acid was dissolved in dilute sodium carbonate, heated to boiling, and a strong, hot solution of potassium permanganate added drop by drop until the colour remained permanent for some minutes; the excess of permanganate was then destroyed by the addition of a drop of alcohol, and, after filtration, the filtrate evaporated to a small bulk was acidified with hydrochloric acid.

The bulky, white precipitate which separated at once, was collected, washed well, and crystallised from dilute alcohol.

0.1263 gave 0.2648 CO₂ and 0.0570 H₂O.
$$C = 57.18$$
; $H = 5.01$. 0.1543 ,, 0.3223 CO₂ ,, 0.0679 H₂O. $C = 56.95$; $H = 4.88$. $CH_3O \cdot C_6H_3(CH_3)(COOH)_2$ requires $C = 57.14$; $H = 4.76$ per cent.

Methoxymethylterephthalic acid, when heated in a capillary tube, sinters at about 250°, and melts completely at 267°. It is only sparingly soluble in cold water, but crystallises well from large quantities of boiling water. With ferric chloride, the aqueous solution gives an ochreous precipitate.

In order to prepare this acid, methoxymethylterephthalic acid (3 grams) was boiled with fuming hydriodic acid (30 c.c.) in a reflux apparatus for 2 hours. The liquid, which, on cooling, became filled with crystals, was diluted with water, filtered, and the crystals washed with a little dilute sulphurous acid to remove iodine. In this condition, the crystals are nearly insoluble in water, but if the solution in dilute alkali is heated to boiling and acidified, the acid does not separate at once, and the filtered solution, on slowly cooling, deposits a voluminous precipitate consisting of microscopic needles. The precipitate was collected, washed well, and analysed, with the following result.

0.1512 gave 0.3063 CO₂ and 0.0580 H₂O. C = 55.24; H = 4.26. $OH \cdot C_8H_2(CH_2)(COOH)_2$ requires C = 55.10. H = 4.08 per cent.

Hydroxymethylterephthalic acid melts at 280—283°, and its solution in methylic alcohol gives, with ferric chloride, an intense reddishviolet coloration.

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XXIII.—Researches on Moorland Waters. I. Acidity. By WILLIAM ACKROYD, F.I.C.

MOORLAND waters are consumed at present by over five and a quarter millions of people in Yorkshire, Lancashire, Westmoreland, and Cumberland. Their well known plumbo-solvent action has been considered of such importance as to warrant a Government investigation, the results of which will be found collated by Mr. W. H. Power, F.R.S., in the Supplement to the Twenty-third Annual Report of the Local Government Board, pp. 332-424, and it is there demonstrated from the work of Mr. and Mrs. Atkinson and Drs. Barry and A. C. Houston that acidity and lead dissolving power run parallel to each other. In common with many analysts, I have long associated plumbo-solvent power with acidity, and in an investigation made for the Halifax Corporation concerning Moorland waters from many gathering grounds, I reported to this effect in 1895. References to the question are made in papers by Messrs. A. H. Allen, C. Rawson, and T. Whitaker (Journal of the Society of Dyers and Colourists, 5, 54-71). The question of acidity is undoubtedly of primary importance in considering this class of waters, and the following experiments and observations thereon will, therefore, be of interest.

Method of Estimating Acidity.

The solutions to be dealt with may be under or a little over $10\frac{1}{10000}$ th of normal, and as concentration by the usual methods is objectionable, I have adopted the following course of procedure as being both the easiest and quickest, and the least likely to introduce errors.

To 100 c.c. of the water in a beaker, 1 or 2 drops of alcoholic solution of phenolphthalein are added, and N/100 alkali is run in from a burette until a very slight pink tint is obtained; this gives the total acidity. Through a little more than 100 c.c. of water, air, free from carbonic anhydride, is rapidly aspirated for half an hour; titration of 100 c.c. of the water thus treated gives the residual or organic acidity, the difference between the first and second titrations being the volatile acidity, and as this is very largely, if not entirely, due to carbonic acid, it may be termed inorganic acidity. As alcoholic solution of phenolphthalein, when used as an indicator, is sometimes neutralised by the addition of a little alkali, it is well to mention here the precaution that not more than 1 or 2 drops of such a solution should be used in titrating moorland waters, or somewhat discordant results may be obtained; this effect I have traced to the acetate present in the indicator solvent.

Diffusion.

In my earliest observations of waters taken from places contiguous to moorlands, there was gradual decrease of acidity on keeping; this I was at first at a loss to account for, but it was eventually put down to diffusion; the Winchester quarts containing the waters were kept in a room where they were freely exposed to sunlight, and they were only opened as required for purposes of analysis. In three of these samples, A, B, and C, the following percentage changes were observed.

Acidity	_
ar commy	

Day of testing.	Α.	В.	C.	Average.
1st	100 86 57	100 86 63 42 29	100 	100 86 76 60 42 26 29

A was from a private well not far removed from moorland; B was from another well of the same kind, and C was from a trench 7 feet deep dug into the side of a moor-capped hill of Millstone Grit.*

It was these results which suggested the advisability of rapid aspiration of air free from carbonic anhydride as a necessary part of any method of estimating acidity. As a preliminary trial, distilled water was charged with carbonic anhydride; 100 c.c. took 60·1 c.c. of N/100 alkali, but after aspiration for half an hour only 0·3 c.c. of alkali was required for neutralisation, which was the initial acidity of the distilled

Some other analytical data concerning these samples are as follows. Parts per 100,000.

	Total solids.	NaCl.	Free NH ₃ .	Albuminoid NH ₈ .	N as nitrites and nitrates.	c.c. of N/100 alkali required per 100 c.c.
A	18	8	nil	0·005	0·56	11
B	63	6·4	0·03	0·03	1·2	10
C	10	2·1	nil	nil	—	7·2

It may also be mentioned that all the waters referred to in this paper are of permanent hardness only.

water. A sample of the water C was now sent for and submitted to rapid aspiration for 30 minutes. Its acidity was reduced to 26 per cent. of the original.

Water taken direct from moorland catchwater or stream may exhibit little alteration on aspiration. Thus a water from a clough receiving its supply from the adjacent moorland showed no appreciable alteration by diffusion in 15 days, neither was the effect of aspiration any more marked. Some freshly-collected samples from very peaty gathering grounds gave respectively 14, 11, 5, and 6 per cent. of volatile acidity, calling the total acidity 100. The following figures were obtained with waters from moorland reservoirs.

Acidity.
c.c. of N/100 alkali required per 100 c.c.

Sample.		Total.	Organic.	Inorganic.
D	Centre of large peaty reservoir Small reservoir	5·3	4·1	1.2=22 per cent.
E		1·3	0·8	0.5=38 ,, ,,
F		2·9	2·0	0.9=31 ,, ,,

Configuration of Gathering Grounds.

Some of my observations appear to throw a new light on the somewhat old problem, why one gathering ground should yield waters which acted much more quickly on lead, or, in other words, were so much more acid, than others. This has been a fruitful subject of discussion and of municipal inquiry, in the course of which expressions have been evolved, and have come into use as synonymous with bad and good waters as, for instance, "high" and "low-level" supplies, the former being regarded as productive of epidemics of plumbism. I have found that mere altitude of gathering grounds is not sufficient to account for some of the striking differences observed in these waters. Certainly, one of the worst waters with which I have had to deal is a high-level one, the reservoir being 1300 feet above sea-level, and better waters have been had from reservoirs 860 to 1020 feet high; on investigation, however, it appeared that some of the latter have gathering grounds rising to a higher level than in the former case. The "high" and "low-level" distinction has, therefore, seemed to me of little or no value, and I have come to the conclusion that, other things being equal, it is rather a question of the average gradient of a gathering ground. The reasons for this conclusion are that the acidity is due to the peat through which the water passes, and that there will be less time for solution or the taking up of the acid where

the gradient is a high one than where it is a low one. I have submitted this hypothesis to the test in a comparison of four gathering grounds on like geological strata—the Millstone Grit—with the following results.

Gathering ground.

Reservoir or clough.	Height above sea level.	Gradient.	Total acidity.
G	1830 to 1450 feet	1 in 44	5.8
H	980 ,, 1100 ,,	1 in 23 to 1 in 28	2.2
I	985 ,, 1480 ,,	1 in 12	1.4
J	1075 ,, 1344 ,,	1 in 12	1.0

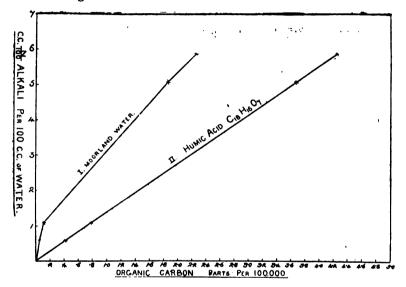
Correlation of Acidity and Absorbed Oxygen Numbers.

Another fruitful source of speculation has been the nature of the acidity of moorland waters. The earliest idea attributed it to mineral acids; now it is put down to peaty acids or, to be more precise, to humic acid. It appeared not unlikely that moist combustion combined with organic acidity determinations might throw further light on the subject, as, for example, some direct relation between the absorbed oxygen numbers and those for organic acidity, on the assumption that the organic acidity represents the presence of a carbon compound of definite composition. Forschammer's permanganate process was employed, the length of the time allowed being 4 hours. The following observations are for waters from widely different moorland sources.

		Pa	rts per 100,0	000.
Sample.		Organic acidity.	Absorbed oxygen.	Calculated organic carbon.
	From a large service reservoir of public supply Another supply of inferior quality From the feeder to a reservoir of com-	0.6 1.1	0·021 0·045	0·050 0·108
	pensation water; running	5.1	0.77	1.848
0	Mountain stream	1.4 {	By interpolation Found	} 0.125 0.15

The absorbed oxygen is here converted into organic carbon by using Sir E. Frankland's factor 2.4. This step was checked by referring back to his analysis of a moorland water, made for official purposes, and of which I had a duplicate sample, O. The organic acidity was 1.4; this gives 0.125 part of organic carbon per 100,000 by interpolation, as against 0.15 part returned in the analysis.

The direct relation looked for only appears in the first two observations. Afterwards, as the acidity increases and the yellow colour deepens, the carbon appears to increase abnormally, as shown in curve I. in the diagram.



The general assumption that the acidity is due to humic acid is somewhat wanting in precision, seeing that some half-dozen humic acids have been found of late years. The basicity of two have been ascertained, namely, Detmer's octobasic acid, $C_{50}H_{54}O_{27}$ (Watts' Dictionary, 7, 648), and Berthelot and André's tribasic acid, $C_{18}H_{16}O_7$ (Abstr., 1891, 1089). The curve for the carbon of the latter approaches nearest to my observations for moorland waters (curve II, diagram); yet it is so far away from it that one is warranted in concluding that the organic acidity of moorland waters is due to an acid or acids of lower equivalent than that of the humic acids whose basicity has been ascertained up to now.

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XXIV.—The Nutrition of Yeast. Part I.

By ARTHUR L. STERN, D.Sc.

SOLUTIONS in which yeast grows freely and ferments vigorously, always contain, besides a fermentable sugar, certain inorganic salts and nitrogenous organic compounds required for the growth and development of the yeast.

The composition of yeast ash indicates that the inorganic constituents are chiefly potassium and magnesium phosphates; small quantities of calcium, silicon, sulphur, and iron are also usually present. A. Mayer (Untersuchungen über die alkoholische Gährung, Heidelberg, 1869), who examined the nutritive value of a large number of salts, concluded that magnesium and potassium phosphates could supply all the inorganic nutriment required by yeast. There is, however, considerable conflict of evidence amongst later investigators as to the necessity for any other inorganic food. Lintner (Lehrbuch der Bierbrauer, p. 427) says sodium and iron are not necessary; H. Molisch (Bot. Centr., 1894, 167) says iron is necessary, but that calcium is not; Wehmer (Beitrage zur Kentniss einheimischer Pilze, p. 158) disputes the necessity for iron; whilst Leyffert (Zeitschr. fur das ges. Brau., 1896, 318) states that yeast degenerates in the absence of calcium salts.

The necessity for sulphur in some form or other is generally assumed, although it does not appear to have been ever proved.

Mayer (loc. cit.) also examined the nutritive value of a number of nitrogenous substances, and found that the most suitable were asparagine, allantoin, carbamide, and diffusible peptones; ammonium salts were not very useful; colloidal albuminoids, like white of egg, fibrin, and casein, were useless, as also were nitrates. These deductions are in general agreement with those of later observers, amongst whom may be mentioned Matthews (Jour. Inst. Brewing, 1897, 369), Ehrich (Der Bierbrauer, 1895, 145, 161, and 177), and Wahl and Hanke (Amer. Brewers' Rev., 7, 32); the latter state that yeast exerts a selective influence on the nitrogenous constituents of malt worts, assimilating most of the amides, and only small portions of the peptones and albuminoids.

Whilst a fairly general agreement prevails that certain substances are necessary for the growth and development of yeast, yet very little is known as to the amount required, or of the effect which a variation of the amount and proportion of these substances produces on the quantity, composition, and properties of the yeast.

Almost the only work in this direction is that of Hayduck (Zeitschrift fur Spiritusind., 1881, 173), who determined the effect of vary-

ing the amount of nitrogenous nutriment on the weight, the amount of nitrogen, and the fermentative power of the yeast. He found that the amount of nitrogen in yeast can vary very considerably, that any increase of nitrogenous nutriment, in the form of asparagine, up to 0.05 gram nitrogen per 100 c.c., results, not only in an increase in the weight of yeast, but also in an increase in the percentage of nitrogen present in it, but any increase in the nitrogenous nutriment above that mentioned neither increases the weight of yeast nor the percentage of nitrogen in it.

Hayduck determined the fermentative power of the yeasts obtained in these experiments, and found that those which contained the highest percentage of nitrogen had the greatest fermentative power.

Kusserow (Brennerei Zeitung, 1897, 317) states that the addition of asparagine to a fermenting solution increases the rapidity of fermentation, but diminishes the yield of yeast; Heinzlemann (Zeitechr. fur Spiritusind., 1897, 296 and 311) makes a similar statement with regard to the rapidity of fermentation.

The effect of varying the amount of inorganic nutriment has never been exhaustively studied, and the statements made on the point are not concordant; Kusserow, for instance (loc. cit.), found that an increase of inorganic nutriment increased the rate of fermentation, the yield of yeast, and its fermentative power, whereas Heinzlemann (loc. cit.) states that it produces no effect on the rate of fermentation. A. G. Salomon and W. de V. Matthews (Journ. Soc. Chem. Ind., 1889, 376) found that the addition of phosphates to malt worts decreased the assimilation of nitrogen and phosphorus by the yeast.

The experiments described in this communication were undertaken with the object of determining the effect which the variation of the amount of inorganic and nitrogenous nutriment produces on the crop of yeast, the assimilation of nitrogen, and the fermentation of the sugar in a given time.

Although some of these problems have been solved by Hayduck, experiments of this nature, to be strictly comparable, must be carried out under absolutely identical conditions; moreover, they acquire additional value when considered in relation to similar work carried out under somewhat different conditions. On this account, it was considered advisable to make the investigation as complete as possible.

Method of Experiment.

The experiments were made in flasks holding rather more than a litre, into which the required amount of mineral and nitrogenous nutriment was introduced, together with 500 c.c. of a 10 per cent. solution of pure dextrose, and the neck of the flask was plugged with

cotton wool. The solution was then boiled for some minutes in order to sterilise the contents, and when cold the yeast was added. The flasks were kept at a temperature of 24°, and well shaken twice a day, when the odour of the evolved gases was noted.

At the end of the stated time, the yeast was filtered off, washed twice with cold water, dried at 100°, and the nitrogen in it determined by Kjeldahl's method. The fermented solution was boiled until the alcohol was expelled, cooled, made up to its original volume, and its optical activity observed, from which the amount of dextrose remaining in solution could be calculated.

The yeast employed throughout this investigation was prepared from a Burton pitching yeast. An Esmarch roll culture was made with wort gelatin, and when, after incubating, the colonies appeared, one was introduced into a Pasteur flask containing sterile hopped wort. Three such flasks were thus seeded, and from these all the yeast used in this investigation was obtained. Neither in their microscopic appearance nor in the flavour of the beer produced by them could any difference in these yeasts be detected, and they in no appreciable way differed from normal Burton yeast.

In order to obtain sufficient yeast for each series of experiments, the fermented wort was decanted from one of the Pasteur flasks, which was then filled up with sterile hopped wort, and well mixed with the yeast sediment; a portion was then poured into a flask containing 500 c.c. of sterilised hopped wort. Fermentation soon began, and when finished the yeast fell to the bottom; the fermented wort was then poured off, and the yeast well mixed with sterilised water. The number of yeast cells in a measured volume of this was counted, and sufficient added to each flask containing the solution to be experimented on, to give 1.5 cells per 1/4000 cubic mm.

Asparagine was chosen as the nitrogenous nutriment, since it is easily obtained in a pure state, and previous observers have found it a very suitable yeast nutriment. It contains 18.7 per cent. of nitrogen.

The mineral nutriment A was prepared by dissolving the ash of yeast in a weak aqueous solution of tartaric acid; B was prepared by dissolving potassium phosphate, magnesium sulphate, and calcium sulphate in water.

A.	B.
Potassium silicate 0.8	Calcium sulphate 3.2
Calcium hydrogen phosphate 1.3	Magnesium sulphate15.9
Magnesium hydrogen phosphate10.5	Potassium hydrogen phosphate80'9
Potassium hydrogen phosphate87.9	

100.0

100.0

EXPERIMENTAL.

Four series of experiments were made with nutriment A. In the first of these, 0.058 gram per 100 c.c. of A was used, and varying amounts of asparagine were added in different experiments. After 7 days, only about half of the sugar was fermented.

In the second series, the conditions were the same, except that the fermentations were continued for 12 days; here, about three-quarters of the sugar were fermented.

In the third series of experiments, the amount of inorganic nutriment was doubled, when as much sugar was fermented in 7 days as was fermented in the second series in 12 days.

In the fourth series, three times the original amount of inorganic nutriment was used, but this had no further effect.

The presence of a considerable amount of unfermented sugar indicates the absence of some essential yeast nutriment.

A series of experiments were then made with inorganic nutriment B, almost identical with that used by Hayduck, and chiefly differing from A by the presence of sulphates. In these experiments, the sugar was almost completely fermented in 7 days, whilst the amount of yeast and of assimilated nitrogen was much greater than in the first series of experiments.

As all other conditions were identical, this must be due to the difference in composition between nutriments A and B, and in order to determine if the presence of sulphates in the one and their absence from the other was the cause of the difference in their behaviour, experiments were made with nutriment A with the addition of sulphate, and with nutriment B with its sulphate replaced by chloride. These experiments proved that the absence of sulphate was the cause of the difference observed. This question of sulphur nutriment is of considerable interest, and will be treated fully in a future paper.

Nutriment B was used throughout the remainder of the experiments. From comparative experiments, it was found that the presence of iron has no effect on any of the functions of yeast investigated in this paper, and cannot be said to be essential to the growth and development of the yeast.

When all the elements necessary for the growth of the yeast were present, it was found that the greatest amount of nitrogen assimilated by the yeast (0.3246 gram) in any experiment was 0.0227 gram per 100 c.c., and, although in some experiments more than six times this amount of nitrogen was supplied, yet the yeast was never able to assimilate more than the amount just mentioned. From experiments made by Nägeli and Löw (Zeitschr. fur das gesammte Brauwesen, 1878, 337) and

others, it has been found that the weight of the inorganic constituents of yeast is approximately equal to the weight of the nitrogen it contains. In round numbers, then, a supply of 0.025 gram per 100 c.c. of inorganic nutriment and of nitrogen as asparagine is as much as the yeast (0.325 gram) is able to assimilate under the conditions of these experiments. This may be called a normal supply.

A.—Effect of Varying the Amount of Nitrogenous Nutriment on:

- 1. The Amount of Nitrogen Assimilated.—When the normal or any larger amount of inorganic nutriment is present, any increase of nitrogenous nutriment above the normal has very little effect on the amount of nitrogen assimilated. The experiments point rather to a decrease of this as the amount of nitrogenous nutriment is increased. If the amount of nitrogenous nutriment is below the normal, the assimilation of nitrogen is much less (Expts. 1, 5, and 6; see p. 207).
- 2. The Percentage of Nitrogen Assimilated .- This is greatest when the supply of nitrogen is least.
- 3. The Percentage of Nitrogen contained in the Yeast.—This does not vary when the nitrogen supply is normal or greater than normal; when, however, the nitrogen supply is below normal, the percentage of nitrogen contained in the yeast is low (Expts. 1, 5, and 6).
- 4. The Percentage of Sugar remaining Unformented.—This does not materially vary, even when the supply of nitrogen is below the normal; if, however, the inorganic nutriment is present in only normal amount, the nitrogen supply being below the normal (Expt. 1), the amount of sugar remaining unfermented is large.
- 5. The Weight of the Yeast Crop.—This is practically unaffected except in the case just noted (Expt. 1), when the yeast crop is small.

B.—Effect of Varying the Amount of Inorganic Nutriment on:

- 1. The Amount of Nitrogen Assimilated.—When the nitrogen supply is below normal (Expts. 1, 5, and 6, p. 207), an increase of the inorganic nutriment has little effect on the assimilation of nitrogen. When the nitrogen supply is normal (Expts. 2, 7, and 8), an increase of the inorganic nutriment causes an increase in the nitrogen assimilation. When the nitrogen supply is above the normal (Expts. 3, 4, 9-23), little effect is produced by increasing the inorganic nutriment, although the trend of the figures indicates a slight increase of nitrogen assimilation as the inorganic nutriment is increased.
- 3. The Percentage of Nitrogen contained in the Yeast.—When the nitrogenous nutriment is below the normal (Expts. 1, 5, and 6), an VOL. LXXV.

increase of the inorganic nutriment causes a decrease in the percentage of nitrogen contained in the yeast. When the nitrogenous nutriment is normal or greater, an increase of the inorganic nutriment has practically no effect on the percentage of nitrogen in the yeast.

- 4. The Percentage of Sugar remaining Unfermented.—When the supply of nitrogen is below the normal (Expts. 1, 5, and 6), an increase of the inorganic nutriment causes a decrease in the amount of sugar remaining unfermented. When the nitrogen supply is normal or greater, an increase of the inorganic nutriment has little effect on the amount of sugar fermented, although the trend of the figures indicates that this causes a decrease in the amount of sugar remaining unfermented.
- 5. The Weight of the Yeast Crop.—This is increased a little by increasing the amount of inorganic nutriment up to 0.25 gram, the effect being most marked when the nitrogen supply was least.

The results of the experiments in which one of the essential elements (sulphur) of yeast food is absent, present much the same general features, but the effect of increasing the inorganic nutriment is much more marked.

So far as might be expected considering the difference in the variety of the yeast used and the differences in the conditions, these experiments are in general agreement with those of Hayduck. It is, however, noteworthy that, whilst Hayduck found that the fermentative power of yeast was proportional to its nitrogen contents, yet in experiments 5 and 6, in which the proportion of nitrogen in the yeast was very low, the fermentation proceeded just as far as in the other experiments.

The most striking result of this investigation may be stated as an enlargement of a proposition which Hayduck deduced from his more restricted work.

Any increase of nutriment beyond a definite limit will not materially increase either the amount of nitrogen assimilated by the yeast, the percentage of nitrogen or the weight of the yeast, or the amount of sugar fermented. This limit is but little greater than the largest amount which the yeast is able to assimilate under the conditions of the experiment.

BURTON-ON-TRENT, October, 1898. TABLE 1.

	-	-
added s yeast.	added sa yeast.	added as added as pear.
9800-0	9600-0	0.0094 0.0096
	: :	
•	-	_
-	-	-
9700-0	0.0036	0.0094 0.0026
0.0807		
		. :
., 0.0587	_	_
		=
=		•
0.0981	_	_
,, . 0.1522	•	•
-		
0.0026 0.0587		
•	•	
"		
		6 6
-	-	
0.0026 0.0587	_	

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XXV.—An Isomeride of Amarine.

By H. LLOYD SNAPE, D.Sc., Ph.D., and ARTHUR BROOKE, Ph.D.

According to Laurent (Annalen, 1844, 52, 356), benzoylazotide, on distillation, yields a mixture of "amarone" and lophine, and we have shown (Trans., 1897, 71, 528) that amarone is tetraphenylazine; a further examination of the products of distillation has shown that a third base, $C_{21}H_{18}N_{2}$, is also present; this melts at 198°, and when subjected to dry distillation yields lophine, $C_{21}H_{16}N_{2}$. Like amarine, with which it is isomeric, it forms salts with one equivalent of acid, and yields a mono-silver derivative, which, on heating, decomposes, with formation of lophine; the silver derivative combines directly with ethylic iodide, hence the base contains an imido-group.

The new base differs from amarine in that it has a much higher melting point; moreover, its chromate does not undergo oxidation when boiled with glacial acetic acid, whereas that of amarine chromate, under similar conditions, yields lophine.

Neither is this base identical with the iso-amarine (melting at 175°) described by Feist and Arnstein (Ber., 1895, 28, 3177), nor with the isomeride of amarine (melting at 259°) mentioned by O. Fischer (Annalen, 1888, 245, 288) as having been prepared by Lorenz Kohler.

The isolation of the base and the preparation of some of its derivatives are described below.

Isolation of the New Base.

- 1. From the Products of Distillation of Benzoylazotide.—The higher distillation products of benzoylazotide, or preferably the residue which is left in the retort when that compound is heated to about 215°, were treated with excess of warm, dilute hydrochloric acid, which dissolved the base and some resinous matter, leaving the tetraphenylazine and lophine undissolved; the base was then precipitated with ammonia, and purified from resinous matter by suspending it in a large quantity of water, adding hydrochloric acid in quantity insufficient to dissolve the whole of the base, and heating the solution by passing in steam; the base was then reprecipitated by ammonia. By repeating this process several times, the resinous matter, which is insoluble in pure water, is gradually removed, as it remains adhering to the walls of the vessel.
- 2. From Mother Liquors.—The alcoholic mother liquors obtained in the preparation of benzoylazotide from benzaldehyde and ammonium cyanide (Trans., 1897, 71, 529), especially when excess of the aldehyde

was employed, were also found to contain the new base; the volatile substances were removed from these liquors by heating with steam, and the dried and powdered residue was extracted with small quantities of alcohol and ether. A crystalline substance melting at 267° was left behind, which, on analysis, proved to be lophine, whilst the new base was extracted by dilute hydrochloric acid from the residue left on evaporating the alcoholic ethereal solution.

It was subsequently found that the most convenient method for extracting the base from the benzoylazotide mother liquors consisted in acidifying with hydrochloric acid, diluting, and distilling with steam; the hydrochloride of the base was thus obtained in solution, whilst the resin, benzoylazotide, and the hydrochloride of lophine remained undissolved. The last-named salt was isolated in octahedral crystals, in one experiment, by crystallisation from chloroform; but generally the residue was subjected to dry distillation at 200—215°, and the residue left in the distillation flask worked up in accordance with the method first given for the isolation of the base. Most of the base used for the experiments recorded in this paper was prepared by the method just described.

In all cases, the hydrochloride was precipitated by ammonia, and the base recrystallised from alcohol, when it was obtained in colourless needles which are soluble in benzene and chloroform, and melt at 198° without decomposing. The alcoholic solution does not become luminous in the dark after treatment with caustic potash (distinction from lophine).

0.1778 gave 0.5500 CO₂ and 0.0990 H₂O. C = 84.36; H = 6.13. 0.1885 , 15.3 c.c. moist nitrogen at 10.5° and 760.1 mm. N = 9.70. $C_{21}H_{18}N_{2}$ requires C = 84.56; H = 6.04; N = 9.40 per cent.

The Hydrochloride, $C_{21}H_{18}N_{2}HCl+H_{2}O$.—A solution of the base in warm, dilute hydrochloric acid, decanted from the amorphous salt which separated on standing, was evaporated in a vacuum over sulphuric acid, when the crystalline salt slowly separated. It has an alkaline reaction, is exceedingly soluble in alcohol and chloroform, very slightly in ether or benzene, and insoluble in carbon bisulphide. It melts at $135-140^{\circ}$ in a capillary tube, and, on cooling, solidifies to a transparent glass. The crystals were dried at 100° until their weight was constant.

0.209 gave 0.0854 AgCl. Cl = 10.05. $C_{21}H_{18}N_{2}$, $HCl + H_{2}O$ requires Cl = 10.07.

The salt was not changed by heating with concentrated hydrochloric acid in a scaled tube for 6 hours at 100° .

Platinochloride, (C₂₁H₁₈N₂)₂,H₂PtCl₆.—This was prepared by

pouring an aqueous solution of the hydrochloride into a solution of platinic chloride, the latter being in excess, and the precipitate crystallised from rectified spirit. The orange-coloured crystals thus obtained begin to lose weight on heating to 220—230°, and fuse with further decomposition at 230—240°. The platinochloride is sparingly soluble in hot water, and rather more soluble in boiling alcohol.

```
0.2246 gave 0.0434 Pt. Pt = 19.33.

0.3741 ,, 0.0726 Pt. Pt = 19.40.

(C_{31}H_{18}N_2)_{29}H_2PtCl_6 requires Pt = 19.30 per cent.
```

Nitrate, $C_{21}H_{18}N_2$, HNO_3+H_2O .—The base was dissolved in dilute nitric acid on the water-bath, and the crystalline crust which formed on the bottom of the vessel, on standing, was redissolved in water; the white crystals which separated from the neutral solution thus obtained had an alkaline reaction, and after drying in a vacuum over sulphuric acid, melted in a capillary tube at about 165°.

```
0.2040 gave 0.4992 CO<sub>2</sub> and 0.1058 H_2O. C = 66.73; H = 5.76. 0.1807 ,, 17.4 c.c. moist nitrogen at 15° and 755 mm. N = 11.2. C_{21}H_{18}N_{2}, HNO_3 + H_2O requires C = 66.46; H = 5.57; N = 11.08 per cent.
```

Chromate.—A solution of the hydrochloride, precipitated by potassium chromate, gave a yellow precipitate which separated from hot glacial acetic acid in well-defined, yellow crystals. The salt was not altered by heating it with glacial acetic acid for 3 hours at 150° in a sealed tube.

Silver Derivative, C₂₁H₁₇N₂Ag.—Freshly prepared silver oxide was dissolved in a dilute alcoholic solution of ammonia, and a solution of the base in rectified spirit poured in in a thin stream, agitating meanwhile. The almost white compound which at once separated was dried at 100°; after being well washed on the filter with alcohol, the light grey powder thus obtained consisted of exceedingly minute, transparent crystals melting and decomposing at 210°. It dissolves in minute quantity in boiling absolute alcohol, but is insoluble in ether, benzene, and light petroleum. When heated with ethylic iodide in a sealed tube at 100°, it dissolves, forming a clear solution.

```
0.1953 gave 0.4466 CO<sub>2</sub> and 0.0756 H<sub>2</sub>O. C=62.36; H=4.30.
```

 $C_{21}H_{17}N_2Ag$ requires $C=62\cdot22$; $H=4\cdot20$; $N=6\cdot91$; $Ag=26\cdot67$ per cent.

Although the relative proportions of base and of ammoniacal silver solution were varied in different experiments, nothing but the monosilver derivative could be obtained; when excess of silver was employed, the yield was practically quantitative.

^{0.2503} , 15 c.c. moist nitrogen at 21° and 764.3 mm. N = 6.83.

^{0.2041} , 0.0540 Ag. Ag = 26.45.

Conversion of the Silver Derivative into Lophins.—On heating this silver compound to fusion, lophine was formed, but no hydrogen or other gas was evolved. Two grams were heated in a paraffin bath to 210°; the transparent, yellow melt, which contained particles of silver in suspension, solidified to a hard mass on cooling; the portion extracted by hot benzene, after being crystallised from alcohol, deposited fine needles sparingly soluble in alcohol, and melting at 267° without decomposition. The alcoholic solution, on adding caustic potash, became luminous in the dark when shaken with air. These properties indicate that the crystals consisted of lophine.

Destructive Distillation of the Base.

On heating the base under diminished pressure, decomposition occurred below 360°, ammonia being evolved and a small quantity of liquid distilling over, the last portions of which solidified on cooling; the residue left in the distillation flask and the solid distillate were dissolved in boiling spirit, from which lophine crystallised out in fine needles; the later crystallisations, which also contained lophine, were digested with warm dilute hydrochloric acid, which dissolved the unaltered base. On recrystallising the insoluble portion from alcohol, more lophine was obtained, and also a small quantity of a colourless substance which separated in thin plates and melted at about 120°; as it volatilised below the melting point of lophine, it was easily separated from the latter by heating the mixed crystals in an air-bath. The crystals of lower melting and boiling point have not been further investigated.

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XXVI.—Studies of the Terpenes and Allied Compounds.

Nitrocamphor and its Derivatives. IV. Nitrocamphor as an Example of Dynamic Isomerism.

By T. MARTIN LOWRY, B.Sc.

In determining the specific rotatory power of nitrocamphor dissolved in benzene, it was noticed that the solution showed a considerably greater levorotatory power when freshly prepared than after keeping, and this was found to be a specific property of the substance; thus a specimen which had been crystallised four times showed a change of rotatory power from $\begin{bmatrix} a \end{bmatrix}_D = -123^\circ$ to -104° in a 5 per cent. solution in

benzene, whilst after four more crystallisations the limits were – 124° and – 104° . Similar changes of rotatory power are exhibited by π -bromonitrocamphor, $C_8H_{18}Br\overset{CH \cdot NO_2}{CO}$, which, like nitrocamphor, contains a secondary nitro-group; but no such changes have been observed in any compounds from which either the nitro-group or the hydrogen atom adjacent to it has been eliminated, that is, the phenomenon is limited to secondary nitro-derivatives of camphor Thus no change of rotatory power is observed in freshly prepared solutions of the aa'-chloronitrocamphor, $C_8H_{14}\overset{CCl \cdot NO_2}{CO}$, the aa'-bromo-

nitrocamphors,
$$C_8H_{14} < \stackrel{CBr \cdot NO_2}{CO}$$
, the salts of pseudonitrocamphor, $C_8H_{14} < \stackrel{C}{C_0} \stackrel{N \cdot OR}{O}$ or the anhydride, $C_8H_{14} < \stackrel{N \cdot O \cdot N}{O} > C_8H_{14}$, nor

does any change occur in such compounds as a-bromocamphor or a-chlorocamphor, from which the nitro-group is absent. The phenomenon depends, therefore, on the presence of a particular group in the molecule, and must be ascribed to chemical rather than to physical changes in the solution; moreover, as these changes take place in all the solvents that have been examined, they must obviously be of the nature of isomeric or polymeric change, and are independent of any chemical interaction with the solvent.

It has already been shown that the salts and the anhydride of nitrocamphor are derived from a pseudo-form of the substance to which the

formula
$$C_8H_{14}$$
 was assigned (Trans., 1898, 78, 997);

these substances have a very high dextrorotatory power, and it is probable that pseudonitrocamphor itself would, in like manner, be dextrorotatory. The changes of rotatory power which take place in freshly prepared solutions of nitrocamphor can, therefore, be readily explained on the assumption that the lævorotatory normal form is partially converted into the dextrorotatory pseudo-form of the nitro-compound, which must then be regarded as *isodynamic*. In the case of π -bromonitrocamphor, both of the isodynamic forms are known in the free state, and, although large differences of rotatory power occur in the freshly prepared solutions, ultimately, a condition of equilibrium is reached which is the same for both.

Cause of Mutarotation in the Sugars.—The spontaneous changes of specific rotatory power which take place in freshly prepared solutions of nitrocamphor and π -bromonitrocamphor are very similar to those which have been observed in aqueous solutions of many of the

sugars and of the acids derived from them. The name of birotation was originally applied to the phenomenon by Dubrunfaut (Compt. rend., 1846, 23, 38) in order to indicate that the transient initial rotatory power of the solution was twice as great as that ultimately attained; this is not so except in the case of glucose, consequently the names of "multirotation" and "paucirotation" have been introduced by Wheeler and Tollens (Annalen, 1889, 254, 310) to indicate that the ratio of the two rotations is a number greater or less than unity. The essential feature of the phenomenon, however, is the change of rotatory power which takes place in the freshly prepared solution, and the term "mutarotation" may, therefore, be used with advantage to include all those cases in which such a change occurs without reference either to the sign or to the relative magnitude of the initial and final rotations.

The phenomenon of mutarotation was first observed by Dubrunfaut (loc. cit.) in an aqueous solution of glucose, and has since been shown to occur in aqueous solutions of eight other sugars, and also in the case of several of the acids and lactones derived from them; a full list of these substances, together with the limiting values of their specific rotatory powers, is given in the accompanying Table I (p. 214). The changes of rotatory power which take place on dissolving gluconic lactone in water were shown by Fischer to be due to its partial conversion into the acid in accordance with the reversible equation C₆H₁₀O₆ + $H_2O \rightleftharpoons C_6H_{19}O_7$; he, therefore, suggested (Bor., 1890, 23, 2626) that, in the case of the carbohydrates also, the phenomenon might be due to hydration, the aldehyde or ketone being converted into a polyhydric alcohol, just as acetaldehyde appears to form an unstable hydrate when dissolved in water; $-CH_{3} \cdot CHO + H_{2}O \rightleftharpoons CH_{3} \cdot CH(OH)_{2}$. This suggestion of Fischer's is that which has usually been adopted to explain the mutaretation of the sugars. The case of π -bromonitrocamphor described in this paper affords, however, a clear case of mutarotation which is caused by isomeric change and not by hydration, and it therefore appears probable that the mutarotation of the sugars is likewise due to isodynamic change, and that when the rotatory power has reached its constant value two dynamic isomerides are present in equilibrium in the solution. In the case of glucose and of lactose, both isodynamic forms appear to have been isolated in an anhydrous condition as a- and y-glucose, and a- and y-lactose; and it has been shown that when dissolved in water the two forms ultimately yield solutions which are similar in every respect, the constant value of the specific rotatory power being the same for both, and intermediate between the values observed in the freshly prepared solutions. The data necessary to ascertain the structure of the dynamic isomerides are not yet available, but it may be suggested

that, in the case of glucose, they would probably be represented by two of the following formulæ.

ҪӉ҈ѺҤ	ÇН₂ОН	ҪӉѹҤ
¢нон	Ċнон	¢нон
¢нон	ÇН	¢нон
¢нон	́ ¢нон	Ċнон
¢нон	ү ¢нон	ĊОН
сно	Снон	снон.

The explanation of the phenomenon of mutarotation given here is essentially different from that recently put forward by Trey (Zoit. physikal. Chem., 1895, 18, 193—218. Compare Lippmann, Ber., 1896, 29, 203—204), who regards the phenomenon as due merely to a change of configuration in the molecule, and not to a change of structure such as that suggested above. Moreover, both Lippmann (loc. cit.)

TABLE I.—Mutarotatory sugars, acids, and lactones.

Substance.	$[\alpha]_D$ initial.	[a] _D constant.	Reference.
a-Glucose	+ 105 ·2°	+ 52 · 50	Parcus and Tollens, Ann., 1890, 257, 164.
β-Glucose	+52.2	,,	Tanret, C.R., 1895, 120, 1060.
γ-Glucose	+ 22.2	,,	Ibid.
a-Lactose hydrate	+82.9	+55.2	Parcus and Tollens, Ann., 1890, 257, 170.
α-Lactose(anhydrous) β-Lactose ,, γ-Lactose ,,	+55°2 +35	,, ,,	Schmöger, Ber., 18, 1917; 14, 2121; 25, 1455.
Maltose	+119	+187	Parcus and Tollens, Ann., 1890, 257, 172.
Fructose	-104	- 92·1	Ibid., p. 165.
Rhamnose	-8.1	+8.6	Schnelle and Tollens, Ann. 1892, 271, 60.
Xylose	+78.6	+19.2	Parcus and Tollens, Ann., 1890, 257, 175.
Galactose	+117.5	+80.8	Ibid., p. 168.
Arabinose	+157	+104.6	Ibid., p. 174.
Fucose	-112	-77	Günther and Tollens, Ann. 1892, 271, 90.
Rhamnonic acid	-7·7°	- 80·1°	Schnelle and Tollens, Ass., 1892, 271, 68.
,, lactone	- 84.8	-84.0	
Gluconic scid	-1.7	+12	Ibid., p. 74.
,, lactone	+ 55°₽ - 10°6	+18.8	71.23 - 01
,, lactone	- 64·8	- 46·8 - 64·0	Ibid., p. 81.
Arabonic acid	-8.2	-45 ·9	Allen and Tollens, Ann., 1890, 260, 212.
Xylonic acid	- 7:0	+17.5	Ibid.

and Tanret (Bull. Soc. Chem., 1896, [iii], 15, 195) represent the mutarotation as being due to the complete change of an unstable into a stable modification of the sugar, and therefore describe β -glucose as being isomeric with a- and γ -glucose; according to the views put forward in this paper, a- and γ -glucose and a- and γ -lactose represent the two isodynamic forms of the sugar, in a state of greater or less purity, whilst β -glucose, β -lactose, &c., do not represent any new form of isomerism, but are merely mixtures of the isodynamic a- and γ -forms. The view that the sugars are isodynamic substances in exactly the same sense as π -bromonitrocamphor and ethylic acetoacetate appears to be entirely new, and the relationship here observed between mutarotation and dynamic isomerism may be regarded as a general one in all cases in which it can be shown that there is no chemical interaction with the solvent such as that which leads to the hydrolysis of lactones in aqueous solution.

Mutarotation of Nitrocamphor.

Ordinary crystalline nitrocamphor melting at 102° may be regarded as consisting of the normal form, its homogeneity being vouched for by the constancy of its initial specific rotatory power, and by its welldefined, crystalline form. The column headed "Initial Specific Rotatory Power" in Table II represents, therefore, the effect of the different solvents on the specific rotatory power of normal nitrocamphor. The most noticeable feature in this column is the sharp contrast which exists between the paraffinoid and the benzenoid series of solvents; with the exception of carbon bisulphide, in paraffinoid solvents the initial specific rotatory power is in all cases less than 40°, the values ranging from 0° in formic acid to -37° in ether; the benzenoid solvents, on the other hand, give much larger numbers, the values ranging from -87° in a 20 per cent. solution in toluene to -124° in a 5 per cent. solution in benzene. The introduction of a side-chain into the benzene nucleus causes a decrease in the rotatory power of the solution; thus, in the case of ethylic benzoate, in which the sidechain and the nucleus are of nearly equal weight, a value is obtained, $[a]_{D} = -50^{\circ}$, which is intermediate between those obtained in the two groups of solvents. A further point of contrast is seen in the effect of concentration on the initial rotatory power; in solutions in chloroform, the values all fall within a degree, but in benzene an increase of 15 per cent. in the concentration of the solution causes a decrease of 24° in the initial specific rotatory power, and a similar decrease of 19° occurs in the case of toluene. The differences between adjacent members of a homologous series are also much greater in the case of benzenoid than of paraffinoid solvents; thus, there is a change of

+18° on passing from benzene to toluene, and a further difference of +7° between toluene and xylene, but the difference between ethylic and propylic alcohols is only +2°, and acetic and propionic acids differ only by -2° . These points of difference are not due to the formation of a polymeric modification of nitrocamphor in the benzenoid solvents, as an increase of concentration would then produce an increase of specific rotatory power in the solution instead of the decrease actually observed, and, moreover, the freezing point of the solution corresponds with a normal molecular weight; they can be best explained as being due to the influence of the normal nitro-group on the benzene nucleus leading perhaps to the production of an unstable additive compound in the solution. This view would be in accordance with the known existence of compounds formed by the loose combination of picric acid with various benzenoid hydrocarbons, and would serve to explain the fact that the anomalous behaviour of benzene and its homologues is most marked in dilute solutions, that is, when the hydrocarbon is present in large excess; it may also be mentioned that pseudo-n-bromonitrocamphor has the same rotatory power in benzene and in chloroform, whilst the normal a-bromonitrocamphor exhibits a difference of 32° in the two solvents. Reference may be made here to the difference between the acids and alcohols of the fatty series, which is especially marked in the lower homologues; thus formic acid and methylic alcohol give a difference of 31°, which falls to 23° in the case of acetic acid and ethylic alcohol, and to 19° in propionic acid and propylic alcohol, the two series converging with increasing molecular weight towards a value of about -15°.

On passing into solution, normal nitrocamphor at once begins to change into the pseudo-form, and as the two forms differ very widely in rotatory power, this alteration of structure is accompanied by a corresponding change in the rotatory power of the solution; within a few days or hours from the time of preparing the solution, the specific rotatory power becomes constant after undergoing a change of from 10° to 24° to the right; the magnitude of the change in the different solvents is given in column 5 of Table II, and is also represented graphically in Fig. 1. It has not been found possible to isolate pseudonitrocamphor in a pure state, and the percentage of each form present in the state of equilibrium cannot, therefore, be calculated with any degree of accuracy; as an approximation, its specific rotatory power may be assumed to be about +180°, a figure which would compare with that of its anhydride, of which $\lceil \alpha \rceil_{p} = +187^{\circ}$ in benzene, and +167° in chloroform, and also with that of its π-bromo-derivative for which $[a] = +189^{\circ}$ (see also p. 235), Taking this value as the rotatory power of pseudonitrocamphor, the percentage of this substance in the state of equilibrium would be about 7 per cent. in both the

parafinoid and benzenoid solvents. From the values given in chloroform solutions, it will be seen that the percentage of the pseudo-form increases with the concentration of the solvent, the change of rotatory power being 12°, 14°, and 16° respectively in 5, 10, and 20 per cent. solutions.

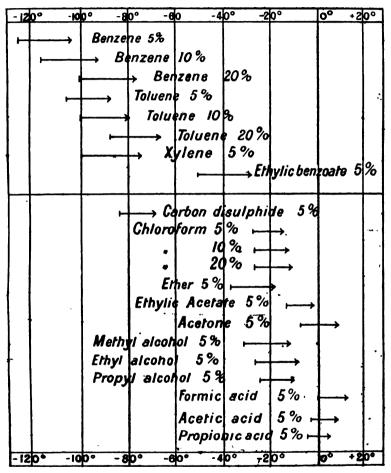


Fig. 1.—Showing magnitude of Change of Rotatory Power of Nitrocamphor in different Solvents.

Velocity of the Isomeric Change.—In most of the solvents examined, the whole course of the change of rotatory power has been followed, and the observations have been plotted in the form of curves, such as those which are represented in Fig. 2, where the specific rotatory

powers are plotted as ordinates, whilst the abscisse represent the time intervals from the moment when the solvent was added to the nitrocamphor. The first reading of the polariscope was usually made within three or four minutes, and observations were then taken every minute during the first half-hour, and subsequently at longer intervals, until constant readings were obtained. The earlier part of the curve is somewhat irregular as a rule, by reason of temperature changes, and the values of the initial specific rotatory power in Table II, which were obtained by exterpolation, are, therefore, given

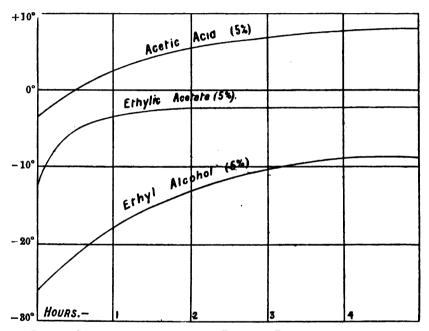


Fig. 2.—Curves showing Change of Rotatory Power of Nitrocamphor with Time.

to the nearest degree, fractional parts of a degree having been omitted. The curves given in Fig. 2 are very similar to those which have been plotted by Parcus and Tollens (*Annalen*, 1890, 257, 160) for aqueous solutions of the sugars, and it is shown under π -bromonitrocamphor that the same equation is applicable to both groups of substances.

Effect of Concentration.—The isomeric change usually proceeds most rapidly in concentrated solutions; thus about a week is required before equilibrium is reached in a 5 per cent. solution in chloroform or benzene at ordinary temperatures, whilst a few hours are sufficient in a 20 per cent. solution. An opposite result was obtained by Hantzsch

and Schultze (Ber., 1896, 29, 2251) in the case of pseudophenylnitromethane, but this may be explained by the fact that this compound is bimolecular, and a dilute solution would, therefore, be most favourable to its conversion into the monomolecular normal form.

Reflect of Temperature.—The velocity of change is very much increased by rise of temperature; a 5 per cent. solution in benzene, which at ordinary temperatures would change slowly during two to four days, was found to have reached a state of equilibrium after it had been warmed to 50° for a quarter of an hour, and then cooled during an equal interval.

Influence of the Solvent.—The interval which elapses before equilibrium is reached is shown for a large number of solvents in column 6 of Table II, whilst in column 8 values are given for the period τ which elapses before the change is half completed. The solvents may be divided into two groups. In solvents containing oxygen, such as the alcohols, acids, ethers, and ethereal salts, equilibrium is reached on the average in about four hours at 15°, the actual periods ranging from a quarter of an hour in acetone to half a day in ethylic benzoate. The hydrocarbons and compounds such as chloroform and carbon bisulphide are much less active, and a period of from two days to a week or more is required before equilibrium is reached in these solvents. A similar result was obtained by Hantzsch and Schultze (loc. cit.), who found that pseudophenylnitromethane changed more slowly in chloroform and in benzene than in ether, alcohol, water, or acetic acid.

Labile Solutions.—From certain observations that have been made with chloroform solutions, it seems doubtful whether the second group of solvents are capable by themselves of bringing about the isomeric change at all. Out of five 10 per cent. solutions that have been examined, three have been found to persist during several days in a labile state without undergoing change, and the same result has also been noticed once in a 5 per cent. solution, but nothing of the kind has been observed in other solvents. Usually, the transference of the solution to the polarimeter tube has proved sufficient to start the change, but in two icases the labile state was found still to persist . however, the change began on warming or shaking the tube. Two curves are given in Fig. 3 (p. 220) to illustrate this; the first curve represents the observations made with a 10 per cent. solution, which showed an almost constant rotatory power during six days, until the labile state was destroyed by warming the tube; the second curve shows the behaviour of a 5 per cent. solution, one portion of which was transferred to the observation tube immediately after it had been prepared, whilst the second portion was not transferred until 16 days later; the initial rotatory power was approximately the same in both

cases, indicating that the solution did not undergo any isomeric change while in the flask, but started at once when poured into the tube. The dotted line in Fig. 3 (a) shows the normal rate of change in a 20 per cent. solution in chloroform. From these observations, it appears probable that a solution of pure nitrocamphor in pure chloroform might be kept indefinitely without

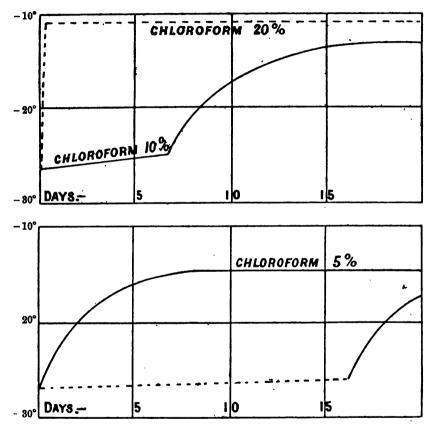


Fig. 8.—Labile Solutions in Chloroform (a) 10 per cent., (b) 5 per cent.

undergoing change; in practice, the solution slowly decomposes and assumes a yellow colour, but that even this decomposition does not necessarily involve isomeric change follows from the fact that a portion of one of the 10 per cent. solutions referred to was kept during 63 days in the graduated flask in which it had been prepared, and, although it had a marked yellow colour, its rotatory power had only fallen from -27° to -22° , instead of the limiting value -13° .

These observations clearly indicate that, at least under certain conditions, a third substance is necessary to bring about isomeric change in the case of nitrocamphor; the results described in the following paragraphs serve to suggest that a trace of basic impurity is, perhaps, essential as a catalytic agent; as an alternative hypothesis, it might be supposed that a trace of the pseudo-form is necessary to start the action; in either case, there is an interesting analogy to the well-known influence of minute traces of water in conditioning chemical change.

Influence of Bases, Acids, and Salts.—It has been shown by O'Sullivan and Tompson (Trans., 1890, 57, 920) that the addition of alkali causes the change of rotatory power of the sugars to take place instantaneously; similar effects are produced in the case of nitrocamphor, as may be seen from the following experiments. quantity of nitrocamphor was dissolved in chloroform containing about 0.5 gram of piperidine per litre; seven minutes after preparing the solution, the specific rotatory power was $[a]_D = -9^\circ$, and no marked change of rotatory power was subsequently observed; the constant rotatory power, so rapidly reached in this case, differs from that previously given in a 5 per cent. solution in chloroform only to an extent which is readily accounted for by the partial conversion of the nitrocamphor into piperidine salt. A similar result was obtained when nitrocamphor was dissolved in absolute alcohol in which sodium had been previously dissolved to the extent of 0.25 gram per litre; in this case, the constant rotatory power had been reached when the first reading of the polariscope was taken three minutes after preparing the solution. In another experiment, however, in which the quantity of sodium was reduced to about 15 milligrams per litre, a very rapid change of rotatory power was observed at first, and a constant value was reached within 12 minutes from the time when the solution was prepared; the quantity of sodium present in this experiment was too small to produce any noticeable effect on the constant rotatory power of the solution, which was found to be $[a]_p = -9^\circ$, the normal value in a 5 per cent. solution in alcohol. No effect of this kind is produced by acids; the addition of 3.5 grams of concentrated hydrochloric acid per litre did not cause any increase in the velocity of change of a 5 per cent. solution of nitrocamphor in alcohol. Neutral salts act similarly to free bases, but less strongly; the addition of 0.7 gram of sodium chloride per litre to a 5 per cent. solution of nitrocamphor in alcohol was found to reduce the period of change from 5 hours to less than an hour.

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$$C_8H_{14} < \begin{matrix} \begin{matrix} \begin{matrix} & \\ & \\ & \end{matrix} \end{matrix} \begin{matrix} & \\ & \end{matrix} \\ + \text{ HOEt} = C_8H_{14} < \begin{matrix} \begin{matrix} & \\ & \\ & \end{matrix} \begin{matrix} & \\ & \end{matrix} \begin{matrix} & \\ & \end{matrix} \\ + \text{ NaOEt.} \quad \text{In these} \end{matrix}$$

equations, the sodium salt is represented as being partially converted by the alcohol into sodium ethoxide and nitrocamphor, on the one hand, and, on the other, into pseudonitrocamphor and sodium ethoxide : these changes, which, of course, would be incomplete and reversible. might be expected to take place with much greater velocity than the simple isomeric change, and it may even be questioned whether the latter is capable of taking place at all apart from such 'catalytic agents.' The interactions which are here assumed to occur in an alcoholic solution of nitrocamphor are strictly analogous to the hydrolysis of a salt into its acid and base, which is most marked in dilute aqueous solution, and when either acid or base is feeble, for example, KCN + H₂O = KOH + HCN. Similar equations may be used to explain the action of the nitrogen bases, but here the change would be analogous to the dissociation of ammonium chloride in the gaseous state, or of aniline acetate in solution in benzene. The influence of neutral salts may be explained as dependent on the 'ratio of distribution' of the base between the nitrocamphor and the acid of the neutral salt. important to notice that these catalytic agents do not disturb the

TABLE II.—Mutarotation of nitrocamphor.

O. larget	Con-	Specific	rotatory [a]D.	power,	Period.	Tem-		4 . 2
Solvent.	centra- tion.	Initial.	Final.	Diff.	r eriou.	pera- ture.	τ.	$k_1 + k_2$
Benzene ,,, Toluene ,,, Xylene Ethylic benzoate. Carbon bisulphide Chloroform ,,, Ether Ethylic acetate Acetone Methylic alcohol.	5 10 20 5 5 5 5	-124° -116 -100 -106 -100 -87 -99 -50 -88 -27 -27 -27 -37 -13 -7 -81	-104° -98 -77 -87 -79 -66 -75 -28 -68 -15 -11 -18 -2 +8 -12	20° 23 28 29 19 21 24 22 15 12 14 16 19 11	4 days 4 days ½ day ½ day ½ day ½ day ½ day 2 days 1 week 6 hours 2 hours 1 hours 3 hours	15° 16 18 20 18 17 20 17 17 13 16 16 18 14 20 16	0.5 h.	0 038 0 68 0 17 0 18 0 20 0 036 0 20 0 12 0 026 0 017 0 48 2 4 4 1 1 6 2 1 6
Ethylic ,, Propylic ,, Formic acid Acetic ,, Propionic ,,	5 5 5 5 5	- 26 - 24 ±0 - 3 - 5	-9 -10 +12 +8 +5	17 14 12 11 10	5 hours 2 hours 3 hours 5 hours 2 hours	15 17 15 13 14	1.1 h. 0.5 h. 0.7 h. 1.0 h. 0.8 h.	0·74 1·6 1·2 0·81 2·7

equilibrium between the isodynamic forms of nitrocamphor, as it has recently been assumed by Schiff that agents of this kind are capable of effecting the complete conversion of ethylic acetoacetate into one or other of its isodynamic forms; this point will be referred to again later.

Mutarotation of m-Bromonitrocamphor.

Through the kindness of Dr. Kipping in providing me with the necessary material, I have been enabled to extend the investigation of nitrocamphor by studying its π -bromo-derivative. The introduction of the bromine atom does not produce any great difference in chemical properties, but completely alters the physical properties of the substance, the most important result being that the pseudo-form is rendered much less soluble and can readily be isolated, whilst it is still possible to isolate the normal form. The condition of equilibrium can, therefore, be approached from either side, and as the rotatory power of the two forms can be determined, the exact percentage of each when equilibrium is reached can be ascertained.

π-Bromonitrocamphor was prepared and examined by Lapworth and Kipping (Trans., 1896, 69, 304), and was described by them as being trimorphous, the three modifications melting at 108°, 126°, and 142°. Two of these forms were submitted to crystallographic measurement, and the axial ratios and the drawings of the crystals are given in the paper referred to. From the results obtained in studying nitrocamphor, it appeared to be possible that the three crystalline modifications might include the normal and pseudo-forms of the substance, and they were, therefore, submitted to polarimetric investigation in order to ascertain the nature and magnitude of any changes which might take place after dissolving them.

The orthorhombic form, melting at 142° , is readily obtained in good crystals from solution in chloroform; when it is dissolved in benzene, the value of $[a]_D$ changes from $+188^\circ$ to -38° in a 3·33 per cent. solution at 13° ; in a 5 per cent. solution in chloroform at 14° , the limits were $+189^\circ$ to $+31^\circ$; the magnitude of the change is, therefore, very large, being two or three times as great as that recorded in any previous case. The high dextrorotatory power of this modification indicates that it is the *pseudo*-form, whilst its purity is vouched for by its definite crystalline form, since the isodynamic forms are not isomorphous. That the salts are derived from this modification of the substance is shown by their similar dextrorotatory power, that of the hydrated potassium salt, $C_{10}H_{18}BrNO_8K + 2H_2O$, being $[a]_D = +221^\circ$ in a 3 per cent. aqueous solution at 15° .

The tetragonal form, melting at 108°, is difficult to isolate in any quantity, as it does not begin to separate until after the ortho-

rhombic form, when the solution in chloroform is allowed to evaporate, but the crystals can be readily distinguished and picked out mechanically. When dissolved in benzene, this modification shows a change of rotatory power from -51° to -38° in a 3:33 per cent. solution at 15° ; it, therefore, resembles nitrocamphor both in the magnitude and in the direction of the change and must be regarded as the *normal* form of the substance.

The third modification, melting at 126°, separates from a hot solution in spirit as a crystalline powder; when dissolved in benzene, a specimen of this form showed a specific rotatory power changing from +150° to -39°, and it must, therefore, be regarded as a mere mixture of the normal and pseudo-forms similar to that which is obtained on allowing a solution in chloroform to evaporate to dryness. Similar mixtures are almost always obtained when crystallisation takes place rapidly, and it is only by obtaining the substance in well-defined crystals that the purity of the two forms can be ensured.

When brought into contact with a solvent, the different modifications of π -bromonitrocamphor yield solutions which are ultimately identical; in each case, the same constant rotatory power, $[a]_D = -38^\circ$, is reached; this affords a proof that the equilibrium is the same in each case and corresponds to a mixture of 1 part of the pseudo-form with 17 parts of the normal. The production of such an equilibrium has already been indicated in connection with the different modifications of glucose and of lactose, and also, somewhat imperfectly, in connection with the acids and lactones referred to in Table I. The changes of rotatory power of normal and pseudo π -bromonitrocamphor in solution in benzene are represented graphically in Fig. 4.

Normal and pseudo- π -bromonitrocamphor differ widely in physical properties; they crystallise in different systems, their melting points differ by 34°, and the specific rotatory powers by 239°; the difference in solubility is also very marked, for whilst the normal form dissolves instantly in cold chloroform, the pseudo-form only dissolves slowly on boiling. In general, the normal form shows a behaviour which indicates a less solid cohesion; thus it has a lower melting point and a greater solubility and is much softer than the pseudo-form.

Form of the Mutarotation Curves.—The change of π -bromonitrocamphor from the normal to the pseudo-form, or vice versa, is a monomolecular action, and might, therefore, be expected to proceed according to an equation of the type

$$dx/dt = k_1(x_0 - x_t) - k_2x_t$$

which, when integrated, becomes

$$k_1 + k_2 = \frac{1}{t} \log \frac{x_0 - x_\infty}{x_t - x_\infty},$$

where k_1 , k_2 are the velocity-constants of the isomeric change in the two directions, and x_0 , x_t , and x_∞ are the quantities of one of the forms at times 0, t, and ∞ . This equation has already been applied by Küster to the isomeric change of the two hexachloroketocyclo-

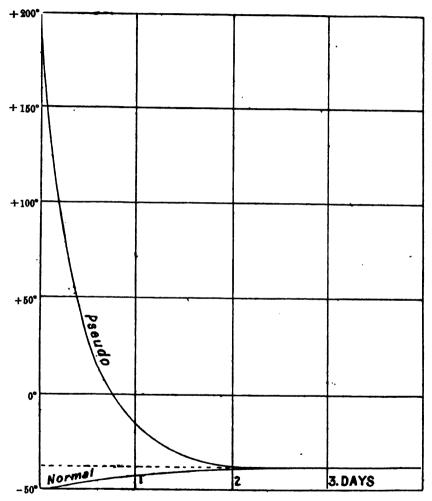


FIG. 4.—CHANGES OF ROTATORY POWER OF PSEUDO- AND NORMAL π-ΒROMONITROCAMPHOR IN BENZENE (8'88 PER CENT.).

pentenes (Zeit. physikal. Chem., 1895, 18, 171), and by Trey to the mutarotation of the sugars (ibid., p. 198). In the case of nitrocamphor and π -bromonitrocamphor, the most convenient unit of measurement is that given by the specific rotatory power of the

solution, and if a_0 be used to represent the rotatory power of the solution when first prepared, a_t that at time t, and a_{∞} the constant value of the rotatory power, then the equation may be written

$$\frac{1}{\epsilon}(k_1+k_2) = \frac{1}{t} \left\{ \log (a_0 - a_\infty) - \log (a_t - a_\infty) \right\},\,$$

where ϵ represents the base of the natural system of logarithms, and has the value 2.7183, whilst k_1 and k_2 are the velocity-constants of the isomeric changes in the two directions, and represent the proportion of each that undergoes isomeric change in the course of one hour. In Table III, the values of the constant $\frac{k_1 + k_2}{\epsilon}$ in the case of

Table III.—Showing change of rotatory power of pseudo-π-bromonitrocamphor in a 5 per cent. solution in chloroform at 14°.

4.0			$k_1 + k_2$		
t (hours).	a _t .	Observed.	Calculated.	Difference.	•
0 h. 0'2 h. 0'5 h. 1'0 h. 3'0 h. 5'0 h. 7'0 h. 24 h. 72 h. 81 h. 96 h. Limit 168 h.	+ 188·5° 187·3 188·3 169·0 156·0 146·0 84·5 87·3 85·8 84·0 81·3	157·2° 156·0 152·0 153·7 125·7 114·7 53·2 6·0 4·5 2·7 0	157·8° 156·4 154·8 150·8 137·7 125·7 114·9 53·2 6·0 4·0 3·2 0	-0.8° -1.7 -1.2 ±0.0 ±0.0 +0.2 ±0.0 ±0.0 -0.5 -0.5	0.0080 0.0166 0.0165 0.0197 0.0198 0.0197 0.0197 0.0191 0.0184

a 5 per cent. solution of pseudo- π -bromonitrocamphor in chloroform are given in the sixth column, and their constancy shows that, after the first hour, the change proceeds quite regularly according to the monomolecular law; the values given in the fourth column for $a_t - a_{\infty}$ are calculated from the equation

$$\log (a_t - a_{co}) = 0.1981 - t \times 0.0197,$$

and show a very satisfactory agreement with the observed rotations, the differences in each case being less than 2° . In Table IV, values are given for both the normal and pseudo-forms of π -bromonitrocamphor

TABLE IV.—Showing change of rotatory power of pseudo- and normal x-bromonitrocamphor in a 3.33 per cent. solution in benzene.

& (hours).	aı	$a_{\ell} - a_{\infty}$.	$(k_1+k_2)\epsilon$.	(k ₁ +k ₂)€ (corr.).	Temperature.
0 h. 0·5 h. 1·0 h. 1·5 h. 8·5 h. 5·0 h. 7·0 h. 8·7 h. 27·0 h. 29·0 h. 81·7 h. 48·6 h. Limit 99·3 h.	(+188·4°) +184·0 +179·7 +175·0 +158·2 +145·2 +129·5 +116·0 +25·7 +18·7 +10·7 -17·5 -88·0	(226·4°) 222·0 217·7 213·0 196·2 183·2 167·5 154·0 63·7 56·7 48·7 20·5 0	0·0170 0·0170 0·0173 0·0178 0·0184 0·0187 0·0192 0·0204 0·0207 0·0210		15° C.
			0.0188 Mean value	0:0210 Mean value	
0 h. 1 h. 25 h. 48 h. 72 h. 118 h. Limit 144 h.	(-51·4°) -50·7 -47·2 -48·7 -42·7 -40·0 -87·5	(18·9°) 18·2 9·7 6·2 5·2 2·5	0.0062 0.0078 0.0059 0.0063		13°
			0.0064 Mean value		

in a 3.33 per cent. solution in benzene; in the case of the pseudo-form, the velocity-constant $\frac{k_1+k_2}{\epsilon}$ in column 4 shows a steady increase as the action proceeds, but this is due almost entirely to the slowness of the isomeric change during the first hour or two, and the later part of the curve gives a satisfactory agreement, as is seen from the constancy of the numbers given in the fifth column, which are calculated from the formula $\frac{k_1+k_2}{\epsilon}=\frac{1}{\epsilon}\left\{0.3700-\log\left(a_{\epsilon}-a_{\infty}\right)\right\}$. Under comparable conditions, the velocity-constant $\frac{k_1+k_2}{\epsilon}$ should be the same for both modifications of a substance, but it is only rarely that this agreement can be realised experimentally; in Table IV, the mean

value 0.0188, in the case of the pseudo-form, is three times as great as the value, 0.0064, obtained in the case of the normal form; this difference may be accounted for in part by the difference of 2° in temperature in the two experiments, but it is probable that some other points of divergence existed between the conditions in the two experiments.

If 0.0188 be taken as a mean value for $\frac{k_1 + k_2}{\epsilon}$, then $k_1 + k_2 = 0.0511$,

and since $k_1: k_2 = 226 \cdot 4: 13 \cdot 9$, $k_1 = 0 \cdot 0481$ and $k_2 = 0 \cdot 0030$, where k_1 is the velocity-constant of the change from pseudo- to normal, and k_2 that of the change from normal to pseudo-; thus, under the conditions of the experiment, 4.8 per cent. of the quantity of the pseudo-form present in the solution would undergo isomeric change in one hour, and only 0.30 per cent. of the normal form.

In the case of nitrocamphor, the changes of rotatory power are too small to give a good result on calculating the velocity-constant from the separate observations, but in Table II the period τ which elapses before the change is half-completed is given in column 8, and from this the constant $k_1 + k_2$ has been calculated for each solvent from the formula $k_1 + k_2 = \frac{\epsilon}{-} \log \frac{1}{2}$.

Comparison with the Nitroparaffins.

It was, I believe, first suggested by Dr. Armstrong in the year 1892 (Proc., 1892, 101), that the salts of the nitroparaffins are derived from a hydroxylic modification of the substance, and not directly from the nitro-compound. This suggestion was verified shortly afterwards by the experimental work of Nef (Annalen, 1894, 280, 263; Ber., 1896, 29, 1218), and since then a number of attempts have been made to isolate the hydroxylic form of various nitroparaffins. Labile crystalline modifications of phenylnitromethane, C₆H₅·CH₂·NO₂, and parabromophenylnitromethane, CoH2Br·CH2·NO2, have been prepared by Hantzsch and Schultze (Ber., 1896, 29, 699 and 2256) by acidifying an aqueous solution of the sodium salt with mineral acids, and the same method has been successfully used by Konowaloff in the case of ω-nitromesitylene, C_aH_aMe_e·CH_e·NO_e, diphenylnitromethane, C_6H_5 $CH \cdot NO_2$, isopropylphenylnitromethane, C_3H_7 $CH \cdot NO_2$, and other secondary nitroparaffins (Ber., 1896, 29, 2193). These labile forms appear to consist largely of the dynamic isomeride from which the salts are derived, but π -bromonitrocamphor seems to be the only nitro-compound of which the two isodynamic forms have been obtained in well-defined crystals of ascertained purity, and submitted to crystallographic measurement (L. and K., loc. cit.). The results

obtained in the two series of nitro-compounds differ in several important respects, and the experiments described in the following paragraphs are, therefore, given in the form of a comparison.

Action of Acids on Aqueous Solutions of the Salts.—The labile pseudo-forms isolated by Hantzsch and Schultze were prepared by the action of mineral acids on a solution of the sodium salt, whilst organic acids, such as carbonic and acetic, on account of their slower action, were found to give either the normal form or a mixture of the two. As this method appeared to afford a ready means of preparing pseudonitrocamphor and normal m-bromonitrocamphor, attempts were made to isolate these. On acidifying a dilute solution of potassium π-bromopseudonitrocamphor, a crystalline powder was obtained which showed an initial specific rotatory power $[a] = +116^{\circ}$ in a 3.33 per cent. solution in benzene; the product was, therefore, a mixture containing only 30 per cent. of the pseudo-form. Moreover, on attempting to isolate pseudonitrocamphor by the action of mineral acids on a solution of one of its salts, a mixture was again obtained in every experiment, the proportions of the two forms being approximately the same as that in which they exist in solution; in one experiment, a known weight of nitrocamphor was dissolved in aqueous potash, precipitated with hydrochloric acid, drained on a filter-pump, and immediately dissolved in a known volume of alcohol; the solution gave a constant rotatory power, $[a]_D = -9^\circ$; the first reading of the polariscope was obtained within 15 minutes from the time when the acid was added to the salt solution, and no change was subsequently observed. If the pseudo-form be assumed to be the first product of the action, the production of a mixture of the two forms can be readily explained as due to the catalytic influence of the salts present during precipitation (compare p. 221), but it is also possible that both forms are produced directly from the potassium salt by the action of the acid, without being first thrown down in the pseudo-form.

Nature of the Isomeric Change, Complete or Incomplete.—It has been stated by Hantzsch and Schultze that the conversion of the pseudo-into the normal nitroparaffins is complete, that is, that the isomeric change is non-reversible; "whilst thus the groups -CH₂·CO- and -CH:C(OH)— are both stable to a certain extent in the free state, of the groups -CH₂·NO₂— and -CH:NO₂H, the first alone is stable" (ibid., p. 2267). This statement is directly opposed to the equilibrium which has been shown to exist between the two forms of nitrocamphor and π -bromonitrocamphor, and is also contradicted by the statement of Konowaloff (loc. cit.), that the labile pseudo-form of xylylnitromethane, which only differs from phenylnitromethane by the presence of two additional methyl groups in the benzene nucleus, is converted into a mixture of the normal and pseudo-forms, containing also a

small amount of the corresponding aldehyde. It appears, therefore, to be more probable that, even in the case of phenylnitromethane and parabromophenylnitromethane, an equilibrium is established between the two forms in solution and in the liquid state, although the quantity of the pseudo-form may be too small to produce any marked coloration with ferric chloride.

Action of Ferric Chloride.—In almost every case of dynamic isomerism that has been studied up to the present, the formation of a coloured ferric salt has been made use of to distinguish the hydroxylic modification, and it has even been made the basis of rough quantitative In the case of nitrocamphor and m-bromonitromeasurements. camphor, this test is not available, as both isodynamic forms give the same coloration with ferric chloride; in order to make sure of this result, crystals of normal and pseudo-π-bromonitrocamphor were crushed and dissolved in equal quantities of cold spirit, and a drop of alcoholic ferric chloride was immediately added to each; not the slightest difference could be detected between the two solutions. either in the depth of colour or in the velocity with which it was produced. This unusual behaviour is most readily explained as being due to the accelerating effect of ferric chloride on the isomeric change, an effect which has already been shown to be produced by neutral salts; it would, therefore, appear that, under the influence of the ferric chloride, equilibrium is reached during the second or two that is required for the development of the coloration.

Action of Nitrous Acid on Nitrocamphor.—It has been stated by Hantzsch and Schultze that, when suspended in ether, all pseudonitro-compounds and their derivatives yield a sky-blue coloration if acted on with hydrogen chloride or acetic chloride. This does not occur in the case of nitrocamphor, but a similar coloration can be produced by the action of nitrous acid. If a drop of dilute sulphuric acid is added to an aqueous solution of potassium pseudonitrocamphor and potassium nitrite, a transient blue colour is produced, which rapidly passes to green and then to yellow; the ultimate product is a yellow oil, which decomposes almost explosively when heated, giving off a considerable quantity of gas and leaving a solid cake of camphorquinone. From analogy to other secondary nitro-compounds, it is probable that the blue substance is the pseudonitrol, and that this passes by loss of 2NO into camphorquinone, as shown by the formulæ

$$C_8H_{14} < \stackrel{CH \cdot NO_2}{CO} \quad \rightarrow \quad C_8H_{14} < \stackrel{C}{CO} \stackrel{NO_2}{NO} \quad \rightarrow \quad C_8H_{14} < \stackrel{CO}{CO}.$$

The blue coloration observed by Hantzsch and Schultze must obviously be due to the nitrous acid which is liberated by the decomposition of the unstable pseudonitroparaffins.

Molecular Weights.—It has been shown by Hantzsch and Schultze that pseudophenylnitromethane is largely bimolecular, and that when it is dissolved in benzene the molecular weight, as determined from the freezing point of the solution, falls slowly from 210 to 141 during the period that elapses before equilibrium is reached; the molecular weight of the normal form, calculated from the formula C, H, NO, is 137. A similar decrease of molecular weight has been shown to occur in a freshly diluted solution of formaldehyde (Escheweiler and Grossmann, Annales, 1890, 258, 103). On making an experiment with pseudow-bromonitrocamphor, the freezing point of the freshly prepared solution was found to be 0.492° lower than that of the benzene used as a solvent; when the solution had been brought to a condition of equilibrium by keeping it at atmospheric temperature during 6 days and then momentarily warming to the boiling point, the depression of the freezing point was 0.552°, the difference between the two values being no greater than that which might be produced by the evaporation of the benzene. The concentration of the solution was found to be 2.946 grams per 100 grams of benzene, and the calculated molecular weight of the substance was 261; from this, it may be concluded that both the isodynamic forms of π-bromonitrocamphor are monomolecular, the theoretical value for a single molecular proportion being M = 271.

A determination of the molecular weight of nitrocamphor in solution in benzene, by the freezing point method, gave the value M = 208 (calc. 197).

The Crystallisation of Dynamic Isomerides.

Crystallisation from Solution.—The behaviour of n-bromonitrocamphor affords a good illustration of the laws which govern the crystallisation of isodynamic substances, and as these do not appear to have been previously discussed, a short account of them is given here. For each form there will be a true solubility which is independent of the isomeric change, but as the isomeride is also present in the solution when equilibrium is reached, the quantity of the substance ultimately dissolved, or the apparent solubility, will always be Thus, every gram of pseudo-r-bromonitrocamphor is in equilibrium in solution with 17 grams of the normal form, and the apparent solubility will, therefore, be 18 times as great as the true solubility, whilst for the normal form the ratio will be 18/17. In the ease of x-bromonitrocamphor, the apparent solubilities of the two forms are very nearly the same, as a mixture of the two is usually obtained on crystallisation; that of the normal form, however, is slightly the larger, as the pseudo-form is always the first to separate from solution; for the sake of definiteness, it may be assumed that the true solu-

bilities of the normal and pseudo-forms are in the ratio of, say, 19:1, in which case the apparent solubilities would be in the ratio of 19:17. On allowing a solution of π -bromonitrocamphor in chloroform to evaporate, the pseudo-form is observed to separate first, and as the isomeric change always proceeds in such a direction as to maintain the equilibrium, the whole of the substance can be obtained in this form if the crystallisation is sufficiently slow. If, however, evaporation takes place more rapidly, the quantity of the pseudo-form in the solution will decrease, and, when the proportion falls to less than one-twentieth of the total quantity of substance in solution, the normal form will begin to separate, and both forms will then crystallise out side by side; for this reason, it has been observed that the normal form only separates in the last stages of the evaporation, and it is only the complete disappearance of the solvent that saves it from being re-dissolved and converted into the less soluble pseudo-form.

In the case of a substance like nitrocamphor, in which the form that predominates in solution is the first to separate, there will not be any marked decrease in the proportion present in the solution unless the crystallisation is extremely rapid, and even then the pseudo-form can only separate in a very small proportion, and would appear merely as an impurity in the normal form. For this reason, it is very easy to obtain normal nitrocamphor in a pure state, and no indication is obtained of the presence of the pseudo-form in the crystals even when the substance separates from solution very rapidly.

Fusion.—When π -bromonitrocamphor is carefully fused on a glass slide and allowed to cool, crystallisation sets in, and when examined under a microscope between crossed Nicols, the slide is seen to be covered with a brilliant, microcrystalline figure; the appearance of the image varies considerably, but radiating lines of minute vacuum bubbles, caused by the contraction of the substance on solidification, are usually present, and appear to be somewhat characteristic of the substance. When examined with an objective of higher power, biaxial interference figures are seen, which show a + double refraction; the substance that crystallises out under these conditions is, therefore, the pseudo-form, since the normal form gives a uniaxial interference figure with, double refraction (L. and K., loc. cit.); the separation of the pseudo-form from a mixture which probably consists chiefly of the normal form, is a somewhat striking illustration of the difference in their mutual solubility, and recalls the similar result obtained on crystallising from solution. Under ordinary conditions, a mixture of the two forms is obtained on cooling the fused substance, just as a mixture is obtained on rapid crystallisation from solution; a specimen that had been fused in a test-tube and rapidly cooled showed an initial specific rotatory power $[a]_{D} = +3^{\circ}$ in a 3.30° per cent. solution in benzene at 17°, and therefore contained 23 per cent. of the pseudo-, and 77 per cent. of the normal form; this result does not indicate the composition of the fused substance, but since the pseudo-form is the first to crystallise, it may be regarded as giving a maximum limit to the percentage of this in the liquid product.

After fusion, all the modifications of π -bromonitrocamphor remelt at 126° (L. and K., loc. oit.), and this temperature, therefore, must represent the point at which the solid pseudo-form can exist in stable equilibrium with the liquid mixture. At this temperature, the solubility of the pseudo-form in the fused normal form must be exactly equal to the percentage in which it exists in equilibrium with it in the liquid state; in the case of π -bromonitrocamphor, this point, which may be called the "equilibrium temperature," lies 16° below the true melting point of the pseudo-form. The true melting point of normal π -bromonitrocamphor, which is given by Lapworth and Kipping as 108°, lies below the equilibrium temperature; but it is somewhat difficult to observe this melting point, as the fused substance rapidly undergoes isomeric change and is converted into the solid pseudo-form, after which it melts again at 126°.

When fused nitrocamphor is allowed to cool, it does not crystallise, but solidifies in an amorphous condition, indicating that the mutual solubility of the two forms is greater than in the preceding case. The initial specific rotatory power of a recently fused specimen was found to be $[a]_{p} = -7^{\circ}$ in a 5 per cent. solution in chloroform at 17°, corresponding with the presence of about 10 per cent, of the pseudoform; as the forces of crystallisation do not, come into play, it may be assumed that these numbers correspond also with the composition of the fused substance. The condition of equilibrium in solution is reached, on the average, when about 7 per cent. of the substance is in the pseudo-form, and this experiment shows that, at a temperature some 80° higher, the proportion of the pseudo-form present in the fused product is not materially greater, since the figure given above is probably too high on account of the formation of the anhydride during fusion. The presence of both normal and pseudo-nitrocamphor in the liquid substance, and their great mutual solubility, affords a ready explanation of the large amount of oil that is obtained in preparing it, for a relatively small amount of a third substance, present as an impurity, would suffice to prevent the mixture from crystallising.

Limits of Stability.—The term "stability limit," or "apparent melting point," has been introduced by Knorr (Annalen, 1896, 293, 70 and 88) to indicate the temperature at which the solid substance undergoes isomeric change, the product being usually a liquid mixture of the two

In the case of normal *m*-bromonitrocamphor, the substance only melts when heated rapidly to a temperature of 108°; when heated more slowly, it is converted into the solid pseudo-form, and then melts at 126°; for this substance, the stability limit is probably just below the true melting point. In the case of normal nitrocamphor, the observed melting point is by no means sharp or well-defined, and may be regarded as merely a stability limit. For pseudo-x-bromonitrocamphor, the stability limit is identical with the 'equilibrium temperature' at which the substance remelts after fusion, but this will not necessarily be so in other cases; thus there would be a definite stability limit or apparent melting point for pseudo- as well as for normal nitrocamphor, but there is no equilibrium temperature for this substance, as it does not crystallise again after fusion; thus the equilibrium temperature always represents a reversible change, whilst the stability limit represents a non-reversible change in the case of one of the isodynamic forms, and often in the case of both. The instability of the solid pseudo-forms of phenylnitromethane and parabromophenylnitromethane can readily be explained by means of the stability limits and the equilibrium temperature; as isomeric change takes place at the ordinary temperature, the stability limits of both pseudo-forms must obviously lie below the atmospheric temperature, but whilst parabromophenylnitromethane has an equilibrium temperature at 60°, and therefore passes without melting into the solid normal form, that of phenylnitromethane is below the atmospheric temperature, and a liquid is produced as the change takes place.

Vaporisation.—So far as I have been able to ascertain, the isodynamic forms described in this paper are quite stable in the crystalline condition; it must, however, be remembered that a very small quantity of solvent would be sufficient to convert a large amount of the more into the less soluble form, and the complete conversion of (e.g.) normal into pseudo-x-bromonitrocamphor might even be effected by the vapour of a solvent; moreover, the conversion of the labile into the stable form must, in any case, take place more or less rapidly by a process of sublimation. Just as in the case of solubility, there will be a true and an apparent vapour pressure, and the labile form will be that which has the greater apparent vapour pressure; in the case of \u03c4-bromonitrocamphor, this is evidently the normal form which has the greater apparent solubility and the lower melting point: the following experiment appears to show that this is also the case with nitrocamphor, and that the conversion of the normal into the pseudo-form actually takes place by a very slow process of sublimation.

It was noticed that a highly purified specimen of nitrocamphor, when kept in a stoppered bottle for several months, acquired a sweetish

smell, whilst the sides of the bottle became clouded over with a thin, white sublimate; the amount of substance thus formed was exceedingly small, but when the bottle was rinsed out with chloroform, a dextrorotatory solution was obtained, which showed a change of rotatory power from right to left; this behaviour is what might be expected from pseudonitrocamphor, and a rough estimate of the initial specific rotatory power gave the value $[a]_D = +150^{\circ} (\pm 10^{\circ})$, which is slightly less than the values previously assumed for this substance and observed in the case of its anhydride; that the sublimate does not consist of this anhydride is shown by the fact that it does not become yellow on exposure to light, and also by the changing rotatory power of the solution. The evidence brought forward here is admittedly slender, but the observation seems to demand some such explanation as that given above.

Dynamic Isomerism.

The isomerism of normal and pseudo-m-bromonitrocamphor and of normal and pseudonitrocamphor is found by experiment to be of such a nature that the two forms can only exist separately in a stable condition when in the solid state, and then only at temperatures below the stability limit; on passing into the fluid state, either by fusion or by dissolution or by vaporisation, a reversible isomeric change sets in, and after a longer or shorter period of time a state of equilibrium is reached in which equal numbers of molecules of the normal and pseudo-form undergo isomeric change in any given interval of time. For this well-defined type of isomerism, it appears advisable that the term "dynamic isomerism" should be used as being more significant than the other terms which have been proposed, and in order to recall the denamic equilibrium which exists between the isomerides in the fluid state; two substances which behave in this way may be described as being 'isodynamic,' or they may be referred to as 'isodynamic forms' of one substance (see the article on "Isomerism" by Dr. Armstrong in Morley and Muir's edition of Watt's Dictionary of Chemistry). In the case of m-bromonitrocamphor, equilibrium is reached in solution when 6 per cent. of the substance is in the pseudoform, and the isomeric change from the pseudo- to the normal form must, therefore, proceed 16 times as fast as the change in the reverse direction; from the velocity-constants given on p. 228, it is seen that in each hour 4.8 per cent. of the pseudo-form and 0.30 per cent. of the normal form underwent isomeric change under the conditions of the experiment. In the case of the separate molecules, the structure will at one time be that of the normal form, and at another that of the pseudo-form, but the isomeric change will only take place somewhat

slowly; thus, in the experiment referred to, the average duration of the two phases would be 21 hours and 13 days respectively.

A theory similar in many respects to that of dynamic isomerism was put forward in the year 1885 by Laar in a paper, "Ueber die Möglichheit mehrerer Strukturformeln für dieselbe chemische Verbindung" (Ber., 18, 648-657). In order to explain the fact that many chemical compounds are capable of yielding derivatives of two types, and that conversely many interactions which might be expected to yield isomerides actually give identical products, he assumed that, in all such cases, the 'tautomeric' substance alternated backwards and forwards between the configurations represented by the two alternative structural formulæ, so that at one moment it had the structure represented by one formula, and at another moment that represented by the other. Thus it has been found that the same substance is produced by the action of nitrous acid on phenol and of hydroxylamine on quinone, and Laar, therefore, assumed that the compound was continually alternating between

the phases
$$\bigwedge$$
 and \bigvee . The essential difference between NO

Laar's theory of tautomerism and that of dynamic isomerism consists in the fact that he regards the phenomenon as intramolecular, and not intermolecular, comparing it with the vibration which gives rise to the spectra of incandescent gases and contrasting it with the equilibrium of dissociation. Two consequences follow from this: first, he regards all isodynamic bodies as homogeneous substances having uniform properties, whereas, in many cases, they can be proved to be mixtures of two isomerides which have different physical properties; second, the phases of the substance could only be separated by cooling to the absolute zero, and so stopping all motion in the molecule, whereas actually it is found to be sufficient in most cases merely to bring the substance into a crystalline form. For this reason, Laar's speculative theory has been generally abandoned, whilst the theory of 'dynamic isomerism' has been verified in a large number of examples.

The term 'desmotropy' was introduced by Jacobson (Ber., 1888, 21, 2628) as an alternative to the word 'tautomerism', but its meaning was narrowed down by Hantzsch and Hermann (Ber., 1887, 20, 2802), who suggested that the term should be used only for those substances of which two solid modifications are known. Two consequences have followed from this: first, a considerable amount of confusion has been introduced in relation to the difference between

polymorphism and dynamic isomerism, and second, according to the present style of nomenclature, π -bromonitrocamphor would be described as 'desmotropic,' whilst nitrocamphor would be merely 'tautomeric,' although the isomerism of the normal and pseudoforms is of precisely the same nature in each case.

Two years previous to the publication of Laar's paper, it was shown by Baeyer (Ber., 1883, 16, 2188) that certain compounds of the indigo-group were capable of yielding two types of derivatives, although they were not themselves known in more than one of the two possible isomeric forms. He, therefore, assumed that one of the isomerides was stable, whilst the other was labile, and went over immediately into the stable form whenever attempts were made to prepare it. Thus, pseudoisatin is not known, although ethyl pseudoisatin is perfectly stable, and, similarly, pseudoindoxyl is known only in the form of derivatives.

Baeyer's hypothesis, to which the name of 'pseudomerism' has been given by Laar (Ber., 1886, 19, 730), may be regarded as contemplating merely a limiting case of 'dynamic isomerism' in which the proportion of one of the isodynamic forms in the state of equilbrium is infinitesimal, so that the isomeric change is practically complete, and proceeds only in one direction.

The credit of recognising the possibility of dynamic isomerism and of applying it to explain the behaviour of substances, such as hydrocyanic acid, which yield two kinds of derivatives, undoubtedly belongs entirely to Butlerow. In a paper, "Ueber Isodibutylen!" (Annalen, 1877, 189, 44), he showed that the products of oxidation of the substance indicated the presence in it of two isomeric hydrocarbons, $\overset{\mathrm{CH}_{3}}{\overset{\circ}{\hookrightarrow}} \overset{\mathrm{CH} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \cdot \mathrm{CH}_{2} \cdot \mathrm{C} \overset{\mathrm{CH}_{3}}{\overset{\circ}{\hookrightarrow}} \overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\circ}{\hookrightarrow}}} \overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\circ}{\hookrightarrow}}}} \overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{C}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}_{3}}{\overset{\mathrm{CH}$ CH_3 $CH \cdot CH_2 \cdot CH : C \leftarrow CH_3$ and and brought forward evidence to show that, in presence of concentrated sulphuric acid, there is a state of equilibrium between the two olefines, the intermediate stage being probably the alcohol or alcohol $_{\mathrm{CH}_{3}}^{\mathrm{CH}_{3}}$ > $_{\mathrm{CH}\cdot\mathrm{CH}_{2}\cdot\mathrm{CH}\cdot\mathrm{C}(\mathrm{SO}_{4}\mathrm{H})}$
 $_{\mathrm{CH}_{3}}^{\mathrm{CH}_{3}}$. He, therefore, sugsulphate, gested that, in other cases, a similar state of equilibrium might exist even in the absence of a catalytic agent, and pointed out that this would fully account for the production of two series of ethers from

hydrocyanic and other allied acids; the recent statement of Knorr (Ber., 1897, 30, 2389), that hydrocyanic acid and other 'tautomeric' liquids are composed of a mixture of two isomerides in equilibrium, is, therefore, identical in every respect with the idea so clearly stated by Butlerow 22 years previously.

To Butlerow belongs also the credit of recognising the importance of catalytic agents in effecting isodynamic change. These substances at least increase its velocity, if they do not underlie the isomeric change, a result which is seen very clearly in the action of bases in accelerating the changes of rotatory power of nitrocamphor and the sugars; in many instances, therefore, they render obvious cases of isodynamic change which would otherwise proceed too slowly to be observed. this class of substances, Butlerow's isodibutylenes obviously belong, and the equilibrium between fructose, glucose, and mannose, when dissolved in dilute potash, affords another example of the same type, and one that is of special interest, as it involves the equilibrium of three dynamic isomerides. Reference may also be made here to the fact that whenever two optical isomerides become isodynamic, either alone or in presence of catalytic agents, an inactive mixture will always be formed. To the former class of substances belong all those which are incapable of being resolved into their optical isomerides by reason of the "chaotic" nature of the molecule, whilst the use of catalytic agents has been illustrated by Holleman in the action of dilute potash on d-phenylglycollic acid (Rec. Trav. Chim., 1898, 17, 323) and of acids and alkalis on the tartaric acids (ibid., p. 66), the existence of an equilibrium being indicated in the latter case between the dextro-, lavo-, and meso-acids. The marked contrast observed between the behaviour of solutions of nitrocamphor when dissolved in chloroform alone, and when in presence of a trace of piperidine, serves to suggest the question as to whether a catalytic agent is not essential in all cases of isodynamic change; in some instances, at least, this appears to be so, but in the fluid state the condition of a single dynamic isomeride must be regarded as essentially labile, since the isomeric change might be brought about by the action of a minute trace of alkali from the glass of the containing vessel, and it is possible that a trace of the second isomeride might prove sufficient; in any case, the catalytic agent appears to be of the same order as the trace of moisture that is probably essential in all chemical changes, and may, perhaps, be regarded as supplying the conditions necessary for the production of a conducting circuit in It is, however, of the utmost importance to notice that, whilst catalytic agents have a very great effect on the velocity of isomeric change, they do not produce any marked alteration in the equilibrium which is ultimately established. The assumption made by

Schiff (Ber., 1898, 31, 602) that ethylic acetoacetate could be converted completely into the enolic or ketonic form by the addition of a trace of sodium ethoxide or of piperidine is obviously impossible, and has been completely disproved by the experimental work of Schaum (Ber., 1898, 31, 1964), who has shown that the physical properties of the substance remain unchanged under these conditions; similar results have been obtained in the case of nitrocamphor, and from these it is obvious that, far from causing the complete conversion of the mixture into one of the dynamic isomerides, these agents are exactly those which would most rapidly bring about an equilibrium between the two forms.

A number of cases are known, and have been studied in detail, in which isomerides that are stable at ordinary temperatures become isodynamic when the temperature is raised; the results obtained in these cases are of considerable importance in helping to solve the more difficult problems presented by substances which are isodynamic at ordinary temperatures. Thus, in the case of the stereoisomeric dibromotolanes, it has been shown by Wislicenus (Dekanatsschrift, "Ueber die Umsetzung stereoisomerer ungesättigter organischer Verbindungen ineinander bei höherer Temperatur," Leipzig, 1890) that at 210° an equilibrium exists in which the cis- and trans-forms are present in the proportion of 48:52.

$$(48 \text{ per cent.}) \overset{C_6H_5C\cdot Br}{C_6H_5CB_r} \; \stackrel{C_6H_5\cdot C\cdot Br}{\longleftarrow} \; \overset{C_6H_5\cdot C\cdot Br}{Br\cdot C\cdot C_6H_5} \; (52 \text{ per cent.}).$$

A similar equilibrium, although complicated by secondary actions, occurs in the conversion of ammonium thiocyanate into thiourea,

$$NH_4 \cdot CNS \implies CS(NH_2)_2$$

(Volhard, J. pr. Chem., 1892, [ii], 9, 11). The case which has been studied most fully is, however, that of the isomeric hexachlorocycloketopentenes, described by Küster in a paper, "Ueber den Verlauf einer umkehrbaren Reaktion erster Ordnung in homogenem System" (Zeit. physikal. Chem., 1895, 18, 161); the equilibrium between these substances, which is reached in about 12 hours at 210°, corresponds with a mixture of 61.4 per cent. of the β -cyclopentene with 38.6 per cent. of the γ -compound,

$$(\beta = 61.4 \text{ per cent.}) \begin{array}{c} \text{CCl} & \text{CCl} \\ \text{CCl}_2 & \text{CCl}_2 \end{array} > \text{CO} \begin{array}{c} \text{CCl} & \text{CCl}_2 \\ \text{CCl} & \text{CCl}_2 \end{array} > \text{CO} (\gamma = 38.6 \text{ per cent.}).$$

In all these cases, equilibrium is reached only slowly at 210° , and at ordinary temperatures the isomerides appear to be stable; they can, therefore, be separated by fractional crystallisation, or even by means of chemical agents; thus Küster was able to estimate the quantity of the β -compound in a mixture of the two isomerides by

converting it into the sparingly soluble anilide, $C_5Cl_5O\cdot NHPh$, the γ -compound remaining in solution unchanged.

When the isomeric change proceeds with even moderate rapidity at a temperature of, say, 100°, it will, as a rule, only be possible to separate the two isomerides by crystallisation, as chemical agents are found to have a great accelerating effect on the change; the various modifications of ethylic diacetylsuccinate, studied by Knorr (Annalon, 1896, 293, 70), were separated by fractional crystallisation, and may be regarded as typical of this group; so, too, the ketonic and enolic forms of ethylic anilidobenzylacetoacetate, described by Schiff (Ber., 1898, 31, 205), can be fused several times, or crystallised repeatedly from spirit before equilibrium is reached between the two forms,

and may, therefore, be regarded as belonging to the same class of dynamic isomerides as the diacetylsuccinic ethers.

π-Bromonitrocamphor is an example of a substance in which the isomeric change proceeds at a moderate rate even at ordinary temperatures, so that the two forms cannot be separated by the usual methods of fractional crystallisation. In this case, advantage is taken of the fact that the dynamic isomerides have nearly the same apparent solubility, so that, on allowing a solution in chloroform to evaporate to dryness, the two forms crystallise out side by side, and can be picked out mechanically. This appears to form almost the limiting case in which the dynamic isomerides can be separated, and when the velocity of change is greater, or the substances are liquids at ordinary temperatures, the task must be regarded as practicable only by the application of extraordinary methods.

In some cases, it is possible to prepare the isodynamic forms of a substance by chemical methods, such as those employed by Hantzsch and Schultze, and by Konowaloff in the case of the nitroparaffins (see p. 228), namely, conversion into the sodium salt and acidification with mineral acids. This was done by W. Wislicenus in the case of ethylic phenylformylacetate (*Annalen*, 1896, 291, 147), and the method has recently been applied successfully by Rabe (*Ber.*, 1899, 32, 84) in the case of ethylic ethylidene- and benzylidene-acetoacetates,

$$\begin{array}{cccc} {\rm CH_8 \cdot CO \cdot CH \cdot COOEt} & {\rm CH_8 \cdot CO \cdot CH \cdot COOEt} \\ {\rm CH_3 \cdot CH} & {\rm and} & {\rm C_6H_5 \cdot CH} & ; \\ {\rm CH_3 \cdot CO \cdot CH \cdot COOEt} & {\rm CH_8 \cdot CO \cdot CH \cdot COOEt} \end{array}$$

in the case of nitrocamphor, it was not found possible to prepare the pseudo-form in this way. In connection with the influence which

bases and salts have been shown to have on the mutarotation of nitrocamphor, it is of interest to notice that, in order to separate the enolic forms described by Rabe, it was necessary to use an excess of the mineral acid so as to neutralise, as far as possible, the accelerating effect of the bases in the solution; this result is directly in accordance with the views put forward on p. 221 as to the action of these catalytic agents.

The recent work of Schiff on ethylic acetoacetate is of interest as showing how dynamic isomerides may sometimes be prepared with the help of catalytic agents. In the condensation of benzalaniline with ethylic acetoacetate, he was able to show (Ber., 1898, 31, 601) that in presence of a trace of sodium ethoxide only the enolic form of the additive compound was produced, whilst a trace of piperidine led to the production of the ketonic form. This action was assumed by Schiff to be due to the complete conversion of the ethylic acetoacetate by these catalytic agents into the enolic or ketonic form; the incorrectness of this view has already been referred to, but the influence of the two kinds of bases can be readily explained by means of equations similar to those which have already been used in the case of nitrocamphor, thus:

The assumptions that are here made are (1) that the bases combine more readily with the ether than with its benzalaniline compound, and are, therefore, more effective in bringing about isomeric change in the former substance; the reversed action in the above equations would then be only slight, as is indicated by the dotted arrows; (2) that the

benzalaniline interacts more readily with these basic compounds than with the free ether.

On account of the equilibrium which exists in a mixture of dynamic isomerides, the addition to it of a chemical agent which interacts with only one form will necessarily bring about the complete conversion of the substance into that form. In this way, normal nitrocamphor is immediately converted by alkalis into a salt of the pseudo-form, whilst the anhydride of the latter is produced on heating it; on the other hand, the salts are reconverted into normal nitrocamphor by acidifying a solution and crystallising the product, whilst the action of bromine and chlorine yields the normal bromonitro- and chloronitrocamphors described in Part I. of this paper (Trans., 1898, 73, 986). For this reason, chemical methods cannot be used in studying substances which are isodynamic at ordinary temperatures, and physical methods must be relied on almost entirely. This objection applies also to the use of agents, such as benzalaniline, which yield additive compounds of both types, and it is somewhat surprising that Schiff, after having demonstrated the enormous influence of a mere trace of sodium ethoxide on the interaction, should have been led to regard the formation of the enolic derivative as proving that the ether was itself entirely enolic. It appears highly improbable that the enolic form of the ether should persist in a labile state, without undergoing isomeric change under the influence of the alkaline salts present during its preparation, or in the subsequent distillation, and such an assumption would only be justified after the nature of the ether had been definitely established by physical methods.

The only chemical method that appears to be available for the study of dynamic isomerism consists in the use of ferric chloride as a colourtest for the presence of a hydroxylic modification; in this case, however, no product separates out from the solution, and as only a minute quantity of the substance is converted into ferric salt, the equilibrium between the isodynamic forms is not disturbed to any appreciable extent. The formation of the coloured ferric salt, and, therefore, the depth of the coloration, depend on the 'ratio of distribution' of the ferric oxide between the hydrochloric acid and the hydroxylic modification of the isodynamic substance, and as the latter is usually a very feeble acid, the amount of ferric salt formed will be exceedingly small compared with the quantity of ferric chloride added, unless the hydroxylic modification is present in large excess. The coloration will, therefore, give a rough indication of the extent to which the substance is present in the hydroxylic form, and in this way a reversible action may be made use of to study cases of reversible isomeric change in which unreversible actions cannot be employed. In the case of nitrocamphor and of π-bromonitrocamphor, the test breaks down on account

of the catalytic action of the ferric chloride, and this may be regarded as indicating a limit to the usefulness of the method.

After a substance has been found to exhibit the dual chemical behaviour characteristic of isodynamic compounds, physical methods must be introduced to ascertain whether the case is really one of dynamic isomerism. The separation of two solid modifications of the substance is obviously of importance, since these may prove to be the two dynamic isomerides, but this must not be assumed to be the case without further evidence, as the differences of physical properties may be due simply to polymorphism. In order to establish completely the existence of dynamic isomerism, it is necessary to prove further that the isomerism persists in the liquid state, although it is not essential for this purpose that the isomerides should themselves be isolated; when, however, this can be done, the nature of the isomerism can be best established by examination of the recently-fused substance, or of a freshly-prepared solution, which may show a gradual change of conductivity (Hantzsch and Schultze) freezing point (ibid.), refraction (Knorr), or rotatory power. In other cases, a substance may be proved to be a mixture of dynamic isomerides by means of variations in its physical properties depending on the treatment it has previously received; thus the changes of density which occur in ethylic acetoacetate after it has been distilled (Schaum), may be regarded as affording proof that it is a mixture of isomerides or of polymerides, since the physical properties of a pure substance cannot be dependent on its past history, except in the case of solids. For many of the diketones, a proof of the presence of two or more isomerides has been afforded by the determination of the magnetic rotation by Dr. Perkin (Trans., 1892, 61, 801).

Polymorphism, depending as it does on the different arrangement of similar molecules in the crystal structure, represents a form of isomerism which can only exist in the solid state and disappears immediately on dissolution or fusion; but when, on the other hand, the differences in crystalline form are caused by differences in the structure of the molecule, the distinction between the various forms will persist for a longer or shorter time in the liquid state. The behaviour of the recently fused substance or of a freshly prepared solution affords, therefore, the best criterion in distinguishing polymerism and dynamic isomerism on the one hand from polymorphism on the other; the difficulty of observation would, of course, increase with the velocity of isomeric change, but even when this is too rapid to be detected, the constants of the liquid in the state of equilibrium would be those of a mixture of the two forms, and the composition of the substance might be established in a similar manner to that

by which the constitution of the liquid diketones has been ascertained by Dr. Perkin from their magnetic rotations.

The chief points of difference between the behaviour of isodynamic and of polymorphous substances are due to the time-factor which is always involved in connection with dynamic isomerides. In the crystallisation of polymorphous substances from solution, there is a sharp temperature limit above which one form only can separate in a stable condition, whilst below it another form is stable; this limiting temperature represents the point at which the solubility curves of the two forms intersect, and it is not possible for them to crystallise out together from solution at any other temperature. If the temperature limit lies above the melting point of the substance or the boiling point of the solvent, one form will be known in a labile state only, and the addition to the solution of a crystal of the stable form will be sufficient to convert it completely into the latter. The behaviour of dynamic isomerides differs only from that just described in that the conversion of one form into the other by isomeric change requires a longer or shorter interval of time; the limiting temperature will be that at which the 'apparent solubilities' of the two forms are equal, but on account of the time required for the isomeric change to take place, it will be possible for the two forms to crystallise out together at temperatures considerably removed from this point, if the crystallisation is sufficiently rapid: this behaviour has already been referred to in connection with the crystallisation of π -bromonitrocamphor from chloroform solution, and is in itself sufficient to indicate that the two kinds of crystals differ in the structure, as well as in the arrangement, of the molecules.

In dealing with the solid substances, similar results are obtained, the temperature of change being represented by the intersection of the vapour pressure curves of the two forms. But whereas the change of one form into another takes place at a sharp temperature limit in cases of polymorphism, there will be no such sharp temperature of transformation in cases of dynamic isomerism, unless the isomeric change takes place extremely rapidly. For this reason, the rapid change of crystalline form which is often observed when a substance is fused on a microscope slide and allowed to cool slowly may be regarded as specially characteristic of polymorphism.

In conclusion, I desire to express my thanks to Dr. Armstrong for the interest he has taken in the work described in this paper, and for the help he has afforded in carrying it out.

CHEMICAL DEPARTMENT,

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XXVII.—The Action of Ammonia on Ethereal Salts of Organic Acids.

By SIEGFRIED RUHEMANN.

The ethylic salts of glutaconic acid and its homologues, as shown some time ago (Trans., 1893, 63, 259, 874; and 1898, 73, 350), when treated with ammonia, yield respectively aa'-dihydroxypyridine and the homologues of it which contain an alkyl radicle in the β -position. Attempts to prepare the corresponding γ -substitution products of this dihydroxypyridine have already been made, but they were without result, as the ethereal salts which were required for the purpose could not be obtained by the interaction of the alkyl derivatives of chloroform and ethylic sodiomalonate (Ruhemann, Ber., 1896, 29, 1016). Those pyridine compounds, as well as the derivatives of the dihydroxypyridine with alkyl groups in the γ - and β -positions are, however, formed from the ethylic salts which are produced by the union of ethylic malonate and its homologues with the ethereal salts of the acids of the acetylene series (see Michael, J. pr. Chem., 1887, [ii], 35, 349; and Ruhemann and Cunnington, Trans., 1898, 73, 1006).

The ethylic salts of the acids containing an acetylene linking (I have as yet only used ethylic phenylpropiolate) combine with ethereal salts of β -ketonic acids, such as ethylic acetoacetate and ethylic benzoylacetate, when the mixture is digested with sodium ethoxide. This reaction does not yield ethylic salts of unsaturated ketonic acids, but derivatives of α -pyrone, the union being accompanied by the loss of 1 mol. of alcohol. In using ethylic acetoacetate and ethylic phenylpropiolate, the reaction may be expressed by the following equation.

$$\begin{array}{c} \mathbf{C_6H_5 \cdot C: C \cdot COOC_2H_5 + CH_2} < & \mathbf{COOC_2H_5} \\ \mathbf{C_6H_5 \cdot C: CH \cdot CO} < & \mathbf{COOC_2H_5} \\ \mathbf{COOC_3H_5 \cdot C: CH \cdot CO} > & \mathbf{C_2H_6O.} \end{array}$$

The hope of transforming these compounds into derivatives of hydroxypyridine has, as yet, not been realised.

This paper contains, besides the record of the work done in this direction up to the present, an account of some experiments which have been undertaken with the view of ascertaining whether the formation of imido-compounds takes place when ethereal salts of other saturated polycarboxylic acids are acted on by ammonia, as in the case of propanetetracarboxylic acid (Ruhemann and Cunnington, loc-

cit.). The constitution of the diamidoimide of this acid is, no doubt, CO—CH·CH_o·CONH_o represented by the formula NH CO_CH-CONH, and one may expect that the ethylic salts of those acids which, like the former, contain carboxyl groups united with two neighbouring carbon atoms, will yield analogous substances, as with them the conditions are favourable for the production of a five-ring compound. course of this reaction depends, however, not only on the position of the carbethoxyl groups in the molecule of the ethylic salt, but also on the nature of the other radicles present. Thus, ethylic B-methylpropanetetracarboxylate, when treated with ammonia, does not give an imidoamido-compound, but yields the tetramide of the acid. Further experiments with the view of investigating more closely this influence are in progress.

EXPERIMENTAL.

Action of Ammonia on Ethereal Salts of Saturated Polycorboxylic Acids.

Ethylic β-methylpropanetetracarboxylate,

$$CONH_2 \cdot C(CH_3) < \frac{CH(CONH_2)_2}{CH_2 \cdot CONH_2}$$

which is formed by the union of ethylic citraconate and ethylic malonate, is very slowly acted on by aqueous ammonia, and only a small quantity of the oil disappears after 6 to 8 weeks. The reaction, however, is accelerated, although it remains incomplete, by heating the ethylic salt with absolute alcoholic ammonia at 150° for 2 days; the amide, being sparingly soluble in absolute alcohol, separates out. It crystallises from boiling water in colourless prisms, which begin to decompose at about 255° and melt at 270° with evolution of gas. The following numbers were obtained on analysis.

0.2162 gave 44.5 c.c. of nitrogen at 14° and 762 mm. N = 24.28. $C_8H_{14}N_4O_4$ requires N = 24.34 per cent.

In order to ascertain whether the above difference in the action of ammonia on ethylic propanetetracarboxylate and its homologue is due to the use of the reagent in alcoholic solution and to the temperature, the experiment was repeated with ethylic propanetetracarboxylate under the same conditions. The solid which separated after heating the ethylic salt of propanetetracarboxylic acid with an excess of alcoholic ammonia for two days was found to be the diamido-imide of the acid. Its identity with the product obtained with

aqueous ammonia was ascertained by a comparison of the physical properties and by a nitrogen determination.

0.2032 gave 38.5 c.c. of nitrogen at 17° and 732 mm. $N=21\cdot15$. $C_7H_9N_8O_4$ requires $N=21\cdot11$ per cent.

Ethylic proponopentacarboxylate, NHCO-CH-CONH2, which

reacts with ammonia in the same way as ethylic propanetetracarboxylate does, yields the triamidoimide of the acid, the oil being completely dissolved when left in contact with concentrated aqueous ammonia at the ordinary temperature for 8—10 days. On concentrating the ammoniacal liquor, crystals separate which readily dissolve in boiling water, and, on cooling, crystallise in colourless needles which melt and decompose at 212°.

On analysis, it was found that

0.1975 gave 40 c.c. of nitrogen at 20° and 759 mm. $N=23\cdot13$. $C_8H_{10}N_4O_5$ requires $N=23\cdot14$ per cent.

Ethylic phenylpropanetricarboxylate, C₆H₅·CH CH₂·CONH₂, when treated with aqueous ammonia, yields, as was to be expected, the corresponding triamide; after 4—5 weeks, the oil disappears, and a solid separates which is very sparingly soluble in alcohol but readily in water, and crystallises from the latter in colourless needles which begin to decompose at about 200° and melt at 230° with evolution of gas. The ammoniacal mother liquor, on evaporation, yields a further crop of crystals of the same substance. On analysis,

0.2035 gave 0.4320 CO₂ and 0.1162 H_2O . C=57.89; H=6.34. 0.2068 , 30 c.c. of nitrogen at 19° and 760 mm. N=16.70. $C_{12}H_{15}N_3O_8$ requires C=57.83; H=6.02; N=16.86 per cent.

Action of Ammonia on Ethereal Salts of Unsaturated Polycarboxylic Acids. γ-Phenyl- aa'-dihydroxypyridine.

The starting point for the formation of this dihydroxypyridine is ethylic phenylpropenetricarboxylate, the product of the union of the ethylic salts of phenylpropiolic and malonic acids. The formula

$$\mathbf{C_6H_5} \cdot \mathbf{C} \stackrel{\mathbf{CH} \cdot \mathbf{COOC_2H_5}}{\leftarrow} \mathbf{CH}(\mathbf{COOC_2H_5})_2$$

indicates that this compound may be regarded as ethylic phenyl-carboxyglutaconate, and that, under the influence of ammonia, it would condense to a pyridine derivative. This reaction takes place, yielding ethylic γ-phenyl-aa'-dihydroxypyridine-β-carboxylate. The action of con-

centrated aqueous ammonia on ethylic phenylpropenetricarboxylate is very slow, only a small quantity of the oil being dissolved in the course of 2—3 weeks, but the action is more rapid with alcoholic ammonia at 100°; after several days, a solid separates, which is the ammonium derivative of the pyridine compound. This dissolves in water with the greatest ease, and the addition of hydrochloric acid precipitates a crystalline substance, which is only sparingly soluble in water but readily in ether or alcohol, and crystallises from dilute spirit in colourless prisms melting at 200°. Their alcoholic solution gives a purple coloration with ferric chloride. The result of the analysis agrees with the formula $\frac{\text{COOC}_2\text{H}_5 \cdot \text{C} : \text{C(OH)} \cdot \text{N}}{\text{C}_6\text{H}_5 \cdot \text{C} : \text{CH} - \text{C} \cdot \text{OH}}$

0.2136 gave 0.5070 CO₂ and 0.0980 H₂O. C=64.74; H=5.09. 0.2044 ,, 10 c.c. of nitrogen at 20° and 754 mm. N=5.55. $C_{14}H_{18}NO_4$ requires C=64.86; H=5.01; N=5.40 per cent.

Ethylic phenylpropenetricarboxylate, on hydrolysis with baryta water, yields, as Michael (*J. pr. Chem.*, 1894, [ii], 49, 20) found, phenyglutaconic acid, and this, when saturated in alcoholic solution with hydrogen chloride, is transformed into *ethylic phenylglutaconate*; after 24 hours standing, water is added to the solution, the oil which separates is extracted with ether, and the ethereal layer shaken with sodium carbonate. The substance which remains on evaporating the ether boils at 186—187° under a pressure of 11 mm. It is a colourless liquid, having a density $d \cdot 18^{\circ}/18^{\circ} = 1 \cdot 1017$. The result of the analysis agrees with the formula $C_6H_5 \cdot C:CH \cdot COOC_2H_5 \cdot CH_2 \cdot COOC_2H_5$

0.2122 gave 0.5310 CO₂ and 0.1348 H₂O. C = 68.24; H = 7.05. $C_{15}H_{18}O_{47}$ requires C = 68.70; H = 6.87 per cent.

The transformation of ethylic phenylglutaconate into the phenyl-

dihydroxypyridine,
$$C_6H_5$$
. $CH=COH$, is best effected by heating

it with concentrated aqueous ammonia in a closed tube at 100°. After 2 days digestion, the oil completely disappears; from the yellow solution thus obtained, hydrochloric acid precipitates a crystalline product which dissolves readily in hot glacial acetic acid, but with difficulty in boiling alcohol. From these solvents, it separates in colourless prisms which melt with decomposition at 254—255°. The yield of the dihydroxypyridine is very satisfactory, 5 grams of the recrystallised substance being obtained from 9 grams of the ethylic salt, corresponding with 78 per cent. of the theoretical yield.

The phenyldihydroxypyridine was analysed, with the following result.

0.1955 gave 0.5060 CO_2 and 0.0855 H_2O . C = 70.58; H = 4.85. 0.2646 , 17.5 c.c. of nitrogen at 18° and 755 mm. N = 7.54. $C_{11}H_9NO_2$ requires C = 70.59; H = 4.81; N = 7.48 per cent.

The chemical behaviour of γ -phenyldihydroxypyridine is analogous to that of the β -substituted aa'-dihydroxypyridines. In alcoholic solution, it gives a red coloration with ferric chloride; dissolved in ammonia, it forms, on adding silver nitrate, a yellow silver compound which darkens on warming; the ammoniacal solution turns green on exposure to the air, but the oxidation takes place more slowly than with the dihydroxypyridines which contain an alkyl group in the β -position. It had been pointed out before (Ruhemann, Bor., 1893, 26, 1559) that the β -substituted aa'-dihydroxypyridines have various properties in common with resorcinol, one of them being the formation of fluoresceins. γ -Phenyldihydroxypyridine gives this reaction on fusion with phthalic anhydride; on adding dilute potash to the product formed, a solution is obtained which is green in thin and red in thick layers; the colour is discharged by acids.

y-Phenyl-β-benzyl-aa'-dihydroxypyridine.

The homologues of ethylic malonate, as stated above, unite with ethylic phenylpropiolate with formation of ethylic salts of unsaturated acids, which may be transformed into aa'-dihydroxypyridines with alkyl radicles in the γ - and β -positions.

Ethylic Phenylbenzylpropenetricarboxylate, $C_6H_5 \cdot C:CH \cdot COOC_2H_5$ —The reaction has been carried out with ethylic benzylmalonate, and the union of this salt with ethylic phenylpropiolate effected as in the former case. The mixture of the two compounds does not become warm on adding the sodium ethoxide, but if the mixture be heated at 100° for 12 hours, about one-third of the ethylic salts will enter into combination, and on again digesting the lower boiling portions of the oily product with sodium ethoxide, a satisfactory yield of the additive compound is obtained; this is isolated in the usual manner. It boils at $260-265^\circ$ under a pressure of 12 mm. and is a viscous, yellow oil having the density d $13^\circ/13^\circ=1\cdot1347$.

0.2005 gave 0.5202 CO₂ and 0.1220 H₂O. C = 70.75; H = 6.75. $C_{25}H_{28}O_6$ requires C = 70.75; H = 6.60 per cent.

On hydrolysis, this compound yields phenylbenzylglutaconic acid, the reaction being effected by digesting the ethylic salt with excess of alcoholic potash on the water-bath for 6 hours. The solid residue left on distilling off the alcohol is dissolved in water and dilute sulphuric acid added; effervescence takes place, and the organic acid is precipitated as a very viscous substance which does not solidify even after standing for some time; it readily dissolves in alcohol and in ether. Without further purification, it is transformed into the ethylic salt by saturating its alcoholic solution with hydrogen chloride, and, after 24 hours, adding water to the solution; the oil which separates is then dissolved in ether, the ethereal layer shaken with sodium carbonate, and, after removal of the ether, distilled under diminished pressure.

Diethylic phenylbenzylglutaconate, $\frac{C_6H_5 \cdot C:CH \cdot COOC_2H_5}{C_6H_5 \cdot CH_2 \cdot CH \cdot COOC_2H_5}$, is a yellow oil which boils at 240—241° under a pressure of 10 mm. and has the density d 13°/13°=1·1082.

On analysis, the following numbers were obtained.

0.2037 gave 0.5598 CO₂ and 0.1255
$$H_2O$$
. $C = 74.94$; $H = 6.84$. $C_{22}H_{24}O_4$ requires $C = 75.0$; $H = 6.81$ per cent.

Monethylic phenylbenzylglutaconate is formed along with the former compound, and is extracted from the product of etherification of the acid by the treatment with sodium carbonate. On adding an excess of hydrochloric acid to the alkaline solution, a viscous, yellow oil is precipitated which partially solidifies in the course of a few days; the solid product is collected with the aid of the pump, washed with very dilute spirit, and purified by recrystallisation from the same solvent. The colourless prisms thus obtained melt at 98°.

The analytical data agree with the formula

The neutral solution of the monethylic salt in ammonia gives, with silver nitrate, a white precipitate of the corresponding silver salt which is not acted on by light. It was analysed after being dried in a vacuum.

0.2335 left, on ignition, 0.0585 Ag.
$$Ag = 25.05$$
. $C_{20}H_{19}AgO_4$ requires $Ag = 25.05$ per cent.

The transformation of diethylic phenylbenzylglutaconate into phenylbenzyldihydroxypyridine takes place very slowly, 5—6 days heating with aqueous ammonia in a closed tube at 150° being required before 4 grams of the oil entered into solution. The con-

tents of the tube, the ammoniacal liquor, and a small quantity of a crystalline product are freed from ammonia by heating in a vacuum; hydrochloric acid is then added in excess, and the precipitate formed is washed with water and dilute alcohol. The substance crystallises from hot alcohol in faintly-coloured, lustrous plates which melt at 175° to a brown liquid.

The result of analysis agrees with the formula

$$\begin{array}{c} \mathbf{C_6H_5 \cdot C(OH) > N.} \\ \mathbf{C_{-C(OH)} > N.} \end{array}$$

With a drop of ferric chloride, the alcoholic solution gives a purple coloration which is discharged by excess of the chloride. This dihydroxypyridine is oxidised under the same conditions as the others; when its solution in alcohol is boiled, with free access of the air, it first turns green, and then brown. On adding silver nitrate to the substance dissolved in ammonia, a yellow precipitate is formed which darkens on warming.

Formation of a Pyrone Derivatives and their behaviour towards Ammonia.

The ease with which the union of ethylic malonate and its homologues with ethereal salts of acids containing an ethylene or acetylene linking is effected by sodium ethoxide induced me to study the action between the ethereal salts of acids of the acetylene series and those of β -ketonic acids. This investigation has been undertaken especially with the view of transforming the compounds which were expected to be produced in this reaction into derivatives of hydroxypyridine, but, as mentioned in the introduction, α -pyrone compounds are formed which, under the influence of ammonia, do not yield pyridine derivatives.

Ethylic a-Pyrone-a'-methyl- γ -phenyl- β '-carboxylate.

The mixture of ethylic acetoacetate and phenylpropiolate does not evolve heat on the addition of dry sodium ethoxide; the union of the two ethylic salts, however, may be effected by digesting the mixture on the water-bath for 5—6 hours, but, in order to obtain a satisfactory yield of the a-pyrone compound, it is necessary to use a larger quantity of the ethoxide (about 2—3 grams) than in the preparation of the ethylic salts of the polycarboxylic acids. On treating the mix-

ture with an excess of dilute sulphuric acid, crystals continue to separate for some time; these are collected, washed with dilute alcohol, and crystallised from hot alcohol, from which they are deposited as long, colourless needles melting at 104°.

This substance is comparatively stable; it passes over readily at 207—214° under a pressure of 12 mm. with but slight decomposition, as a yellowish oil which quickly solidifies. The pyrone compound is insoluble in water, but dissolves in ether as well as in alcohol, and these solutions do not give a coloration with ferric chloride.

The analytical data agree with those required by the formula

$$C^{\varrho}H^{\varrho} \cdot C \stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:C(CH^{\varrho})}{\stackrel{C:$$

 $3KHO = \frac{C_6H_5 \cdot C:CH \cdot COOK}{CH_2 \cdot COOK} + CH_3 \cdot COOK + C_2H_6O.$

This transformation is effected by alcoholic potash; on adding the latter to the ethylic salt, a red coloration is produced which disappears on boiling. After 4 hours digestion on the water-bath, the alcohol is distilled off, the residue dissolved in water, and hydrochloric acid added; this precipitates a crystalline solid readily soluble in hot water, from which it crystallises in colourless prisms. The compound is characterised as phenylglutaconic acid by the melting point, 154—155°, and by the results of analysis.

0.2035 gave 0.4778 CO₂ and 0.0895 H_2O . C = 64.03; H = 4.88. $C_{11}H_{10}O_4$ requires C = 64.07; H = 4.85 per cent.

The presence of acetic acid in the products of hydrolysis of the pyrone compound was ascertained by the ordinary tests.

Action of Ammonia on Ethylic Methylphenylpyronecarboxylate.—The pyrone derivative dissolves in absolute alcoholic ammonia if left in contact with it for about an hour, and the pale yellow solution deposits a white, crystalline solid which rapidly increases in quantity; this is collected on a filter, washed with absolute alcohol, and dried in a vacuum over sulphuric acid. The following analysis indicates that

the pyrone compound has undergone a transformation which may be represented by the equation

$$C_{6}H_{5} \cdot C:CH \cdot CO > O + 2NH_{8} = \frac{C_{6}H_{5} \cdot C:CH \cdot COONH_{4}}{COOC_{2}H_{5} \cdot C:C(CH_{8})NH_{2}}.$$

0.2044 gave 0.4606 CO₂ and 0.1253 H₂O. C = 61.45; H = 6.81. 0.2025 , 0.4560 CO₂ , 0.1265 H₂O. C = 61.41; H = 6.94. 0.2458 , 20 c.c. of nitrogen at 15° and 766 mm. N = 9.60.

 $C_{15}H_{20}N_2O_4$ requires C = 61.64; H = 6.84; N = 9.59 per cent.

The compound thus produced is very soluble in water, and on heating at 100°, it evolves ammonia and turns yellow. It is characterised as an ammonium salt by the fact that, with silver nitrate, its aqueous solution yields a white, gelatinous precipitate of the corresponding silver salt; this is not acted on by light, and although it turns brown when heated at 100°, it can be dried in a vacuum.

0.2725 left, on ignition, 0.0767 Ag. Ag = 28.14. 0.4090 gave 14 c.c. of nitrogen at 18° and 750 mm. N = 3.89. $C_{15}H_{16}AgNO_4$ requires Ag = 28.27; N = 3.66 per cent.

On adding hydrochloric acid to the aqueous solution of the ammonium salt, a substance is formed which is not the expected pyridine derivative, but is ethylic methylphenylpyronecarboxylate. The acid, therefore, removes 2 mols. of ammonia from the ammonium salt and transfers it into the same pyrone compound from which, by the addition of ammonia, it was produced.

Ethylic a-Pyrone-a' γ-diphenyl-β'-carboxylate.

This is produced in the same manner as the former compound, by digesting a mixture of ethylic phenylpropiolate and benzoylacetate with sodium ethoxide on the water-bath for several hours, using in this case also about 2—3 grams of the ethoxide. The reaction is generally incomplete, a certain amount of the ethereal salts remaining uncombined; their presence often prevents the pyrone compound from crystallising out of the mixture, but the separation can easily be effected by fractionally distilling, under diminished pressure, the oil obtained on adding dilute sulphuric acid to the product of the reaction. First, the unchanged ethylic salts pass over, and then, at about 270°, under a pressure of 12 mm., the pyrone derivative distils as a very viscous, yellowish oil with green fluorescence. This oil, after a short time, solidifies; the solid readily dissolves in ether or alcohol, and crystallises from the latter in well-developed, colourless prisms which melt at 120—121°.

The analytical results correspond with those required by the formula $C_6H_5 \cdot C: CH \cdot CO > O$. $COOC_2H_5 \cdot C: C(C_6H_5) > O$.

0.2021 gave 0.5553 CO₂ and 0.0910 H₂O. C = 74.94; H = 5.00. $C_{20}H_{16}O_4$ requires C = 75.0; H = 5.0 per cent.

The yield of the pyrone compound is very satisfactory, as the unaltered ethylic salts which are contained in the lower fraction of the oil can be transformed into the pyrone by repeated digestion with sodium ethoxide.

The further investigation of the pyrone derivatives described in this paper, and the study of the reactions between ethylic salts of other β -ketonic acids and those of unsaturated acids of the acetylene series, is in progress, and will be published shortly.

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XXVIII.—The Changes of Volume due to Dilution of Aqueous Solutions.

By Edward Bruce Herschel Wade, M.A.

Object of the Paper.

THE object of this paper is, first, to describe an apparatus intended for the study of volume changes consequent on diluting an aqueous solution; secondly, to give an account of experiments performed with that apparatus. The experimental numbers obtained are not intended merely as illustrations of the applicability of the method (though they serve that purpose), but also as accurate values of the change of volume on dilution. The actual change studied in this paper is that which occurs when a certain volume of solution is diluted with an equal volume of water.

I. Review of Previous Work bearing on the Subject.

The method of attacking the problem hitherto invariably employed has been to determine the density of solutions; and the researches carried out may be profitably subdivided into two classes, (a), those the direct object of which is the measurement of the contraction on

dilution, (b), those in which the density was observed for ordinary purposes.

Researches bearing directly on the subject of Contraction.—The first group includes the work of Nicol (Phil. Mag., 1883, [v], 16, 121), Charpy (Compt. rend., 1889, 109, 299), and others. Nicol's plan was to determine the density of a solution of known strength, and then to dilute to exactly half that strength, and redetermine the density. His paper contains a table of contractions obtained in this way. Charpy's densities are carried out to four places of decimals, so that changes of volume less than 1 in 10,000 would escape notice. Marignac (Arch. Gen., 1870, 39, 273) made observations of density to five places of decimals, in order to find the relation, if any, of contraction to heat capacity.

Other Researches bearing on the Subject.—Determinations of density for various purposes have been made by many observers, but it will not be necessary to refer to those which are quoted to less than five places of decimals. Amongst those to be noticed are the results of Gerlach (Zeit. anal. Chem., 8, 279), Marignac, Nicol, Pickering (Trans., 1891), Bremer (Zeit. physikal. Chem., 1888, 3, 423), Kohlrausch and Hallwachs (Ann. Phys. Chem., 1893, 50, 118; 1894, 53, 15), and, later, Kohlrausch (ibid., 1895, 61, 185).

Examination of existing Density Determinations.—In most of the cases quoted, the first obstacle to the employment of the densities in the study of contractions is the way in which the results are stated. To calculate the contraction due to dilution from the data in an ordinary table of densities is a very serious task. Of course an actual error in arithmetic would not be excusable, but most of the tables of density are so constructed that one must have recourse to much interpolation in order to obtain the desired result. Again, when the very inconvenient calculation has been made, the results obtained by different authorities are not very concordant; as an example, Table I (p. 256) gives the contractions of certain solutions as deduced from the tables of Nicol, Pickering, Marignac, and Kohlrausch and Hallwachs. The last two observers have utilised earlier observations by Gerlach and Kohlrausch to complete their tables.

Explanation of Table I.—n= gram equivalents per litre before dilution; n/2= gram equivalents per litre after dilution; V= volume which holds 1 gram equivalent before; 2V= volume which holds 1 gram equivalent after dilution. The figure in the remaining columns are the contractions in c.c. per 100,000 of the diluted solution as deduced from the following authorities. Nicol (N_1) and (N_2) ; Kohlrausch and Hallwachs (K. and H.); Pickering (P); Marignac (M) (loc. cit.).

The discordance amongst the various authorities is perhaps not

TAB	LE	I.
Sodium	chi	loride.

n.	n/2.	V.	2 <i>V</i> .	N_1 .	N ₂ .	K.	М.
1	0.2	1000	2000		31.5	32·5	15
0.8	0.4	1250	2500		22.4	24.4	8
0.6	0.3	1666	3333		14.1	14.7	8.8
0.55	0.275		1 !	16	l		l
0.4	0.2	2500	5000		6.2	7.2	1.0
0.275	0.185			1	l		
0.2	0.1	5000	10000			2.3	1

Sulphuric acid.

n.	n/2.	V.	2 V.	K.	M.	P.
l	0.5	1000	2000	85.5	34.5	27
0.8	0.4	1250	2500	29.6	20.8	24.8
0.6	0.3	1666	3883	23.1	13.5	20.7
0.4	0.2	2500	5000	17.2	5.4	15.6

Cane-sugar.

n. 1 0·8 0·6 0·4	n/2. 0·5 0·4 0·3 0·2	V. 1000 1250 1666 2500	2 <i>V</i> . 2000 2500 3333 5000	35·0 80·0 18·0 9·8	62 82·8 9·3 0	
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surprising if we remember that to establish one value of the contraction by measurements of density involves the errors of four weighings, namely, (1) pyknometer empty, (2) full of water, (3) full of solution, (4) full of diluted solution. Neglecting further errors of temperature and concentration, the sum may very easily surpass one in 100,000. With regard to Kohlrausch and Hallwachs' method of determining the density, which claims a very high order of accuracy, it should be said that it is restricted to solutions whose density is below 1.03, so that, for stronger solutions, they have adopted numbers obtained by less refined methods.

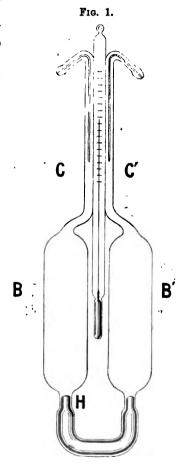
II. The Experimental Method employed in the Paper.

Features of the Method.—The method employed will now be explained without dwelling as yet on details of procedure. The contraction of a solution on dilution with an equal volume of water is observed direct,

in an apparatus constructed specially for that purpose. Attention is fixed on the contraction, and no attempt is made to measure the absolute volumes very accurately. In order, however, to make the results obtained with different pieces of apparatus comparable and of general utility, the results are stated, not as actual contractions, but as contractions per 100,000 c.c. of the diluted solution, and for this

reason some knowledge of the actual volumes mixed is, of course, necessary. It will be shown, however, that a very imperfect knowledge of the absolute volumes suffices for this purpose.

Descriptions of the Apparatus.— Roughly, the apparatus resembles a U-tube whose two limbs are extended into bulbs of nearly equal capacity, BB', Fig. 1. These bulbs are provided with long capillary stems, CC', between which a scale is placed; a few cubic centimetres of mercury, H, fill the bend of the tube. Thus the contents of the bulbs are isolated, as by a door. It was possible, as will be seen, to fill one bulb and stem with a solution. and the other with water. the filling, the water and solution are kept entirely separate by the partition of mercury. To obtain a measure of the contraction due to mixing the water and solution, it is necessary first to set the apparatus upright in a water-bath and read the position of the menisci of water and solution on the capillaries; then to place the apparatus in a horizontal position, so that the mercury barrier no longer intervenes and diffusion takes place, which may be promoted by slight shaking of the mercury; lastly, to



set the apparatus upright once more and take a second reading of the menisci in the capillaries. The difference of the first and second readings is a measure of the contraction due to mixing.

Accessory Apparatus.—Besides the actual contraction apparatus, the outfit consists of a water-bath, stirring-gear, reading telescope and mercurial thermometer. The water-bath was a galvanised iron tank

holding 50 gallons, and the natural fluctuations of this large mass were exceedingly slow, so that it was easy to keep the water at constant temperature by placing a small gas jet under the tank and adjusting the height of the flame when necessary; for such a large water-bath an automatic thermostat is quite superfluous. The stirring-gear consisted of two propellers driven by a large water motor; for the construction of this very efficient apparatus, I have to thank Mr. F. Thomas, of Jesus Lane, Cambridge, who has had much experience in similar work. The thermometer was by Hicks, and gave actual elevations correct to 0·1° and, what was much more important, could be trusted to indicate differences of temperature in the water-bath to within about 0·005°.

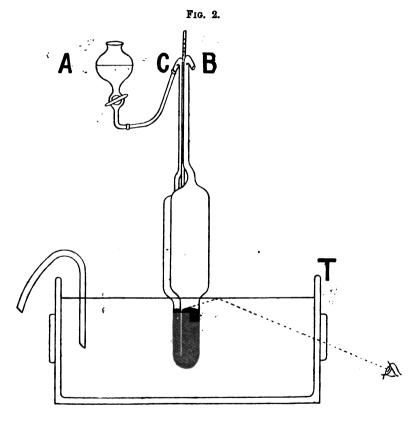
III. The Conduct of an Experiment.

Filling the Apparatus.—At the outset of an experiment, the apparatus has to be filled with water on one side and solution on the other. Some distilled water is well boiled to free it from air, and this water is drawn into the apparatus while hot; to do this, one mouth, C, Fig. 2, of the apparatus is connected with the hot water in the funnel A. By alternately gently sucking and blowing at B, we can gradually fill one bulb with water free from air, without allowing it ever to transgress the partition of mercury. In exactly the same way, the remaining bulb can be filled with hot, boiled-out solution. Throughout the operation, the mercury separates water and solution. When the liquids are cool, the filling has to be completed, and pains must be taken that when the apparatus is vertical the two mercury surfaces are in the same horizontal plane, otherwise the ratio of the volumes of the liquids in the two bulbs will not be a definite one. The operation is referred to as "levelling."

Levelling.—This could be accomplished with the necessary accuracy by placing the apparatus vertically in a shallow glass trough, T, containing water. The water is removed by degrees, and if the observer looks upward obliquely, see Fig. 2, at the surface of the water, he sees the reflections of the mercury menisci descending to meet the real ones as the water is removed. If the two mercury menisci are in one horizontal plane, they will come in contact with their reflections at the same moment; if they fail to do so, water is added to one bulb, or solution to the other, until the test is satisfied. The test was sensitive enough to show a change of 0.05 c.c. in either bulb, which was many times smaller than what was absolutely necessary.

Readings.—We have next to obtain accurate readings of the menisci on the scale of the capillaries. The menisci are brought into such a position that the horizontal cross-wire of the telescope appears to pass

through them both, while the vertical cross-wire grazes the image of the scale; the reading where the horizontal cross-wire intersects the scale is then recorded. To ensure accurate readings, we must observe the following precautions. 1.—The temperature of the water-bath must be kept steady, or else fluctuations must be allowed for, and kept within 0.02°. 2.—The apparatus must be exposed for a sufficient period to this temperature. 3.—Parallax must be avoided. With



regard to the temperature, it could be read with relative accuracy to about 0.005°, and owing to the large capacity of the bath it was usually constant to within about 0.02° for a whole day.*

To ensure that the apparatus had been exposed to this steady temperature for a sufficient period, readings were always continued until they became steady. With the very vigorous stirring employed, the

^{*} This is illustrated in Tables V and VII (pp. 264 and 266), which might be multiplied, and is of the greatest importance. The limit of accuracy is ultimately fixed by the steadiness of the water-bath.

steady state usually sets in in about three-quarters of an hour, and then no further changes can be detected for six hours, except such as correspond accurately with the small and slow changes of the waterbath temperature. This point being settled in preliminary experiments, the apparatus was assumed to be in the steady state when its readings were unchanged during an hour and a half. Parallax was avoided by setting the capillaries vertical, and using a spirit level on the reading telescope.

The Mixing of Water and Solution.—When the reading thus obtained has been entered in the notebook, short lengths of rubber tubing of narrow bore are slipped over the ends of the capillaries, and into these tubes are placed drawn-out pieces of glass tubing. The tips of the glass tubes are now sealed, and the apparatus is ready for the process of mixing. The best way to secure complete mixing of water and solution was found by preliminary experiments with coloured solutions, so that every stage could be watched. The apparatus is set horizontally with the bulb containing the salt solution uppermost. The denser solution descends owing to gravity, and almost without diffusion, so that two layers, one of water and the other of solution. can be distinguished in each bulb. A slight shake of the mercury at this stage makes the mixing almost complete. The mercury is then transferred about 50 times from one bulb to the other, a slight shaking following each transfer. Further mixing will then not alter the reading obtained, and analysis shows that the concentration of the two bulbs is the same. (See section VI.)

Second Reading.—The reading, after mixing, is taken in just the same way as the first, the sealed ends of the glass tubes mentioned above being first cut off. The difference of the readings on the capillaries before and after mixing measures the contraction.

Determination of Concentration.—The concentration was in almost all cases found analytically in preference to working with synthetically prepared solutions; the objection to the latter course was that it would be necessary to dry out the apparatus before each experiment. The carbamide solutions, however, were made up to definite strength and the apparatus carefully dried, instead of using an analytical method. The chlorides were all titrated with silver nitrate, and the oxalic acid and potassium ferrocyanide by potassium permanganate. The strength of sugar solutions was found from their specific gravities with the help of Kohlrausch and Hallwachs' tables.

IV. Standardisation of Apparatus and Solutions.

The section devoted to the reduction of experiments (VI) will show that the necessary data are, (1) the volume of that part of the appa-

ratus unoccupied by mercury, (2) the volume of a portion of the capillaries equal in length to one scale division; from these, a factor (called the apparatus constant) can be obtained which, multiplied into the observed difference of the first and second readings, gives the contraction in cubic centimetres per 100,000. Besides this constant, we need to know the temperature coefficient of the apparatus, that is, the amount by which the reading of the apparatus is affected by a change of 1.0° and also a constant (called the inequality constant) which is defined as the difference in volume of the two bulbs divided by their sum. The significance of this constant is explained in section VI.

Determination of the Volumes of the Bulbs.—This was generally done by weighing the apparatus, first empty, then after the admission of the mercurial partition, and again after filling the remaining space with water. As a control method, the volume of water required to fill the space unoccupied by mercury was drawn in from a calibrated burette, and as another control the same space was completely filled with decinormal sodium chloride, which was then washed out, by repeated washings, into a beaker and titrated with decinormal silver nitrate; the volume of silver nitrate required is equal to the volume of liquid (other than mercury) which is contained by the apparatus. The two control methods were very useful, as after the apparatus was once mounted in its stand, it could not be conveniently displaced for weighing. The capillaries were standardised in the usual way by weighing columns of mercury occupying the greater part of their length and calculating their mean cross-section. The local cross-section was found by calibration with short columns of mercury. A preliminary calibration was always made, and if unsatisfactory the tube in question

 No.
 Apparatus constant.
 Notes.

 1
 12.95
 2.59

 2a
 4.53
 3

 3
 17.91
 4

 4
 10.77
 (10.88 in experiments previous to October 16th, 1897, owing to use of a larger mercury partition.)

 A. 1.
 17.46
 Broken after only six experiments had been made.

TABLE II.

^{*} The formula for this constant is $100,000 \ (\mu_r + \mu_i)/V_\rho$, where μ_r is the mass of mercury in length of right capillary equal to one mean scale unit, μ_i the same for left capillary. ρ density of mercury. V the volume of the apparatus exclusive of that occupied by mercury partition.

was rejected. All these standardisings were repeated at intervals throughout the research, and a complete history of each apparatus was kept. Table II (p. 261) gives the constants of the pieces of apparatus used.

The temperature coefficient of each apparatus was determined over a range of about 10° by reading the levels of the menisci at various steady temperatures. The following table will serve as an example.

TABLE III.
Temp. coeff. of Ton. 3.

Temp.	Reading.			
19·56°	104-260			
19.56	104.260.			
19 <i>·</i> 56	104.260			
19.56	104.260			
19.98)	104.725			
19.96 }	104.71			
19·97 J	104.715			
19.97	104.72			
Therefore, change of re	ading for 0.01°=0.012.			
16·50°	101 -275			
20.17	105.505			

Therefore, change of reading for 0.01°=0.012.

The inequality constant d was found by measuring the volume of each bulb separately in the way already described, and also by filling one bulb with a solution of sodium chloride and the other with water and mixing as in an ordinary experiment; the loss in titre due to mixing gives a value of the inequality. The value of d can also be controlled by making a series of observations of contraction with the solution first in the right bulb; secondly, in the left. If the proper value of d is used in the reduction of these results, the two curves will be identical (see VI.).

Standardising the Volumetric Solutions.—The silver solution was prepared (1) by weighing the pure silver nitrate after exposure for 10 minutes to a temperature of 120°, (2) by titrating against ammonium chloride specially resublimed just before use, (3) by weighing the silver chloride corresponding to a known mass of the solution, (4) by titrating with specially purified potassium bromide.

The titrations for standardising were made both by weighing out the solutions, and also by using pipettes and burettes, the errors of which were accurately known. The permanganate solution was standardised by titration with oxalic acid and ammonium oxalate. When titrating the solutions of potassium ferrocyanide, the permanganate was standardised by means of a carefully recrystallised specimen of that substance.

V. Calculation of the Results.

The calculation of the results is, on the whole, simple. An example follows which it is hoped will make it clear.

TABLE IV.
Sodium chloride.

I.	II.	III.	IV.	٧.	VI.	VII.	VIII.
108.770	108-620	0·150°	19:980°	19 ·9 60°	0.020°	0.126	2.26
IX.	x.	XI.	XII.	a.	ъ.	c.	d.
10.65	10.70	11.23	10.70	1.2	17.91	0.050	0.020

Column I gives the reading on the scale of the capillaries before mixing. Column II, the same after mixing. Column III, the difference. Column IV, the temperature of the water-bath at the time of recording reading in column I. Column V, the same for Column VI, the difference (V-IV). Column VII column II. shows the number in column III corrected for change of temperature, to do which the number in column VI is multiplied by the constant a, and added to the number in column III. Column VIII shows the contraction in cubic centimetres per 100,000; numbers in this column are obtained by multiplying those in column VII by the constant b. Column IX contains the volume of standard solution measured from a burette in order to titrate 10 c.c. (nominal) of the solution whose contraction is found in column VIII. Column X shows this volume corrected for calibration of the burette, and column XI reduces it to gram equivalents per 100,000 c.c. of solution. To obtain column XI multiply the figures in column X by constant 1+c. Finally, column XII corrects for the inequality of the two bulbs. To obtain it, multiply column XI by 1+d if the solution is in the right bulb, and divide by 1+d if in the left.

VI. Discussion of Errors.

The errors attending each operation will be considered separately, and then the question of concordance of results will be raised.

Possible Change of Volume of the Apparatus.—A characteristic error in most volumetric work arises from changes in the volume of the measuring apparatus. In the method described, all the operations can be carried out in a water-bath at constant temperature, and, moreover, a change of volume, even if it occurs, is only significant when it takes place between the initial and final readings. It is to be particularly noted that, as the apparatus is continually under observation during this interval, such a change could scarcely escape detection, and a long experience of the apparatus has not revealed any such change in the course of an experiment. If, however, a change occurred at the time of mixing, it could not be detected in the way described, and, therefore, to test the point, blank observations were made with water in each bulb. The example given shows that no change took place in the volume of the water, even when the apparatus was removed from the bath, and although the mixing was carried out much more energetically than in an ordinary experiment.

TABLE V.

Blank experiment; water in each bulb.

Time.	Temp.	Reading.	Reading reduced to temp. 19 960°.
1 2·30	19·970°	104·715	104·703
2 5·30	19·950	104·690	104·702

Between 1 and 2, the apparatus was removed and mixing carried out.

The difference in the last column is decidedly smaller than could be read with certainty, and corresponds to a change of only about 0.02 in 100,000.

Errors in Standardising.—Even great carelessness in standardising would scarcely affect the results, because the percentage error in the contraction is necessarily equal to the percentage error in the standardising by which it was deduced. The greatest contractions observed were, with very few exceptions, of the order of 40 units, that is, 40 c.c. in 100,000 of the solution. An error of 1 per cent. in standardising would, therefore, cause an error of 0.4 such units, a quantity at most three or four times greater than the least which could be detected with certainty, and the error would be correspondingly less

in smaller contractions. But it is altogether unlikely that the errors in standardising would amount to 1 per cent., as the independent determinations of the volume of the apparatus agree to within about 0.3 per cent., and the standardising of the capillaries are more concordant than that. An example, taken from the standardising of Ton. 4, will illustrate this.

TABLE VI.

Standardisation of Ton. 4.

Date.	<i>v</i> .	V_{H}	Total calc.	Total obs.	μ	μι
February 17	90.7	7.4	98·1	98.0	0.0630	
March 16		_		98.1	0.06321	0.07075
,, 25		6.4		98.2	0.06290	0.07082
,, 26	91 •4	6.2	97.9	98.0	0.06302	0.07067

V is the "water volume" or part unoccupied by mercury, V_H the "mercury volume" or part occupied by mercury. The sum of these gives the whole volume (total calc.); this total may also be obtained by direct observation (total obs.). These totals ought to be constant to within the error of observation, but V and V_H are not necessarily the same in different fillings. After March 25, pains were taken to make V_H always equal to 6.5, otherwise the factor of the apparatus has to be recalculated at every filling; μ_r and μ_l are the masses of mercury in a mean scale unit of the right and left capillaries respectively.

The numbers in Table VI show that the errors due to standardising must be small, and the same conclusion may be drawn from the regularity of the results obtained in different apparatus. See Tables X. XI.

Parallactic Error.—This error is also insignificant. Thus experience showed that if the telescope were put out of adjustment by a considerable distance, and the readings repeated, no sensible change was produced.

Incomplete Mixing.—A possible source of error, and one which undoubtedly was present in the preliminary experiments, is imperfect mixing; in all the final experiments, however, mixing was very thorough, and proved to be complete by analysis. In the example given below, a reading was taken, the contents of the apparatus were then mixed as in an average final experiment, and a second reading was taken; then a second very thorough mixing followed, and a third reading was taken. The second and third readings, reduced to a common temperature, are in agreement, showing that the first mixing was complete.

5.0

22.31

	10 ruusirais	10 thus or all completeness of with the					
Time.	Reading.	Temp.	Reading reduced to temp. 20°335°				
1.0	23.00	20.340° mixed as in	22.99 ordinary final experiment.				
8.0	22:32	20:335	22.89				

mixed again as before.

TABLE VII.

To illustrate completeness of mixing.

The error of inequality of the bulbs appears to be completely avoided by the method of correction described in V, which consists in increasing all the values of concentration in a certain ratio when the solution is in the smaller bulb, and diminishing them when it is in the greater. Great attention must be given, however, to the operation described as levelling (page 258), otherwise the ratio of the bulbs is not the same for the same apparatus in different experiments. The method of correcting was arrived at from a study of Kohlrausch's tables of density, which lead to the conclusion that if, say, $V - \delta$ cubic centimetres of normal sodium chloride are mixed with $V+\delta$ of water, the contraction is sensibly the same as if equal quantities of the two were mixed (provided δ is small), the small deficiency of salt solution being almost exactly compensated for (as far as contraction is concerned) by the small excess of water. But the final concentration will, in one case, be below half normal, and in the other exactly half normal, for both the deficiency of solution and excess of water act the same way on the final concentration. Hence the method of correction. concordance of results by different pieces of apparatus with different inequalities, and using opposite bulbs to contain the salt solution, is considered to justify the correction. For instance, Table XI shows that, within the error of observation, sodium and potassium chlorides satisfy the equation $X = n^b/a$ where X is the contraction on 100,000 cubic centimetres, n the number of gram equivalents in the same, and a, b, are constants. The concordance with this equation is not affected by the apparatus used, or the side of it which contains the solution.

Errors in Titration.—In the greater part of the solutions examined, an error of 0.1 c.c. in the titration would correspond to a change in the contraction which could not be measured.

Error of Temperature.—The most troublesome error is that due to measurement of temperature, and, unlike all the other sources of error, its effect is not proportional to the magnitude of contraction. The greatest percentage effects are, therefore, produced in the dilute

solutions. In spite of the very thorough stirring and continued readings of the apparatus and thermometer, the uncertainty in the temperature of the apparatus (not the thermometer) may have reached 0.01°. Two opposite errors of this magnitude would affect the apparent contraction by about 0.2 unit.

Concordance of Results.—The general concordance of the final results leads to the conclusion that the error in the weakest solutions is about 0.2 unit, and that it may grow to 0.5 in the strongest.* Of course this does not disprove the existence of a systematic error, but such an error, if it exists, would certainly tend to be exposed by using different patterns of apparatus. The five instruments employed varied widely in dimensions, yet no evidence of a characteristic error was found in them.

In the weak solutions of sodium chloride, there is good concordance between the contractions measured directly and those calculated from Kohlrausch and Hallwachs' density tables. In the stronger, the concordance is not so good, but then in such solutions Kohlrausch and Hallwachs have availed themselves of earlier numbers by Gerlach, which are only stated to five places of decimals. A comparison is made in Table VIII.

TABLE VIII.

Comparison of contractions (X) in cubic centimetres per 100,000 observed by the author with those calculated from Kohlrausch and Hallwachs' tables: n is the number of gram equivalents per 100,000 cubic centimetres of diluted solution.

Wa de. 2∙0	X (Kohlrausch and
	Hallwachs) 2.3
6.6	Hallwachs) 2:3
18.0	14.7
	24 · 4
	32.5
	2.0

VII. The Experiments.

Material Employed.—The substances chosen for the measurement of contraction are representatives of the more important classes of compounds. Neutral compounds, which are supposed to remain undissociated in solution, are represented by cane sugar and carbamide;

^{*} In the case of strong solutions of cane sugar and potassium ferrocyanide, the error is somewhat greater, but in these solutions the method of finding the concentration was not so accurate as for the chlorides; and, secondly, the contraction was increasing very rapidly with the concentration, so that errors in finding the concentration were of greater importance than usual.

salts dissociating into two parts, by chlorides of sodium, lithium, and potassium; salts dissociating into three, by chlorides of calcium and strontium; salts dissociating into more than three, by potassium ferrocyanide. Mineral acids are represented by hydrochloric acid, and organic acids by oxalic acid. The purest commercial samples were used, and as far as possible they were recrystallised and their purity confirmed by analysis. Sodium chloride was recrystallised from strong hydrochloric acid, and the acid carefully removed, the salt washed with a little water, and finally ignited. The sample, on analysis, gave Cl = 60.4 per cent.; Calculated, 60.6 per cent. Potassium chloride on analysis gave Cl = 47.8 per cent.; Calculated 47.6 per cent. A best commercial sample of lithium chloride was dissolved in water and filtered from the very slight trace of insoluble matter. The ratio of lithium to chlorine was then determined. Found 1:5.3; Calculated 1:5.04.

The observations marked* in Table XI were obtained with a commercially pure calcium chloride, the remainder with a solution on which special pains had been taken; the latter was made by acting on perfectly limpid crystals of Iceland spar with very pure hydrochloric acid made from redistilled sulphuric acid, and the sodium chloride already mentioned. The spar was in excess, and the solution was filtered from it.

Preliminary Experiments.—Several series of preliminary experiments were made on sodium and potassium chlorides while learning the manipulation; the earlier ones were faulty and discordant, but the later ones may be worth placing on record, although they did not attain the accuracy of the final series.

TABLE IX.

Preliminary observations on KCl, NaCl.

	F			Na	.Cl.	
78.	X.	n.	X.	n.	X.	Explanation.
15·0 15·0	5·0 5·0	84·5 36·5	18·0 21·0	12·5 19·0	4 5 8	n=number of gram equi- valents per 100,000 c.c.
19.0	7.0	45.2	27.0	22.0	8	and X=contraction in
24.4	11.0	47.0	31.0	22.0	8	c.c. per 100,000 of the
24.5	10.0	47.7	29.0	25.0	10	solution due to 50 per
29.0	14.0	48.4	32.0	49.0	29	cent. dilution.
30.0	16.0	50.0	88.0	50.5	88	1
81.0	16.0	50.1	84.0	51.5	88	1
81.5	14.0	51.4	85.0			

The faults known to be still present in these observations were (1) imperfect stirring, with consequent uncertainty of temperature,

(2) insufficient attention to the 'levelling' (see section III.). The first error was removed by the introduction of Mr. Thomas' stirring gear after the series on sodium chloride was completed and that on potassium chloride was about half complete. The second was not properly understood until the close of the two preliminary series, and from that time irregularities disappeared.

The Final Experimental Results.—Tables X and XI give the results obtained when everything was in working order. X represents as before the contraction in cubic centimetres per 100,000 and n the number of gram equivalents in the same; X (calc.) are the numbers deduced from the equation; X (calc.) = n^b/a , which was found to answer well in most cases.

TABLE X. KCl. a = 19.1; b = 1.64.

п.	X (calc.)	X.	T.	n.	X (calc.)	X.	T.
9.50	2.13	2.8	4 R	32.80	16:12	15.8	8 R
12.65	8.38	8.2	8 L	33.45	16.64	16.4	8 R
18 [.] 15	3.60	3.8	3 L	34.40	17.42	17.1	4 R
18:65	6.41	6.1	8 L	37.20	19.81	19.7	3 R
21.3	7.70	7.7	A 1	48 20	30.29	30·6	3 L
24.2	9.79	9.8	3 L	50.0	32.18	31.7	4 L
24.2	9.79	9.9	8 L	52.45	34.6	34.3	A 1
26.25	11.18	11.2	3 R	51.0	83.3	38.0	A 1
27:3	11.8	11.8	4 L	49.2	31.3	31 ·8	8 L
80.60	14.2	14.4	ĀĪ	35.6	18.3	18.2	8 R
30.85	14.58	14.2	3 L				

NaCl. a = 25.0; b = 1.70.

n.	X (calc.)	X.	T.	n.	X (calc.)	X.	T.
9.60	1.87	1.6	3 R	49.30	30.20	30.4	4 I
10.70	2.25	2.3	8 L	49.40	30.29	80.0	4 L
16.82	4.87	4.9	8 L	49.50	80.41	29 · 9	4 I
21.45	7.11	7.1	3 L	50.00	80.08	31.6	3 B
22.60	8.02	8.0	3 L	50.62	31.57	81.4	3 R
89.85	21.04	21.4	3 L	50.90	31.86	31 ·6	4 R
49.10	29.95	29.7	4 R	52.95	34.13	84 ·2	3 L

Numerous observations were made on these salts in order to test experimental error and the influence of the apparatus used. The names of the apparatus appear under T, and letters R, L, indicate whether solution was in right or left bulb. For the remaining

substances, a smaller number of observations have been thought sufficient, and the results are contained in Table XI, using the same notation as before.

TABLE XI.

а	$8rCl_2$ =12.59; $b=1.5$	4.	a:	CaCl ₂ . = 13.275 ; $b = 1.4$	52.
n.	X (calc.)	X.	n.	X (calc.)	X.
12.54	8.90	4.0	9.90	2.50	2.8
12.92	4.09	4.4	10.40	2.65	2.4
18.16	6.90	6.2	12.55	3.52	3.3
19.52	7.71	8.3	15.01	4.62	4.8
29.76	14.76	14.8	24.0	9.44	9.0
32.57	16.96	15.3	30.35	13.49	13.4
46.95	29.80	30.2	49.13	28.02	28.1
47.02	29.86	30.0			

а	Cane sugar. $= 57.15$; $b = 2.0$	0.	a=	LiCl. =19·28; b=1·55	28.
n.	X (calc.)	X.	n.	X (calc.)	X.
13.9	3.38	8.5	13.85	2.87	2.7
24.3	10.33	10.2	20.66	5.29	5.4
3 0·01	15.76	15.8	35.86	12.30	11.0
48.99	42.00	41.6	86.80	12.80	13.0
49.3	42.54	43.4	37.00	12.91	13.2
49.9	43.57	44.5	45.96	18.00	17.5
50.9	45.32	44.7	h		

HCl. $a = 29.45$; $b = 1.49$.			$C_2H_2O_4$.		
n.	X (calc.)	Х.	n.	X.	
16.52	2.21	2.0	15.70	7.2	
24.72	4.04	3.8	20.48	9.1	
26.51	4.48	4.7	30.03	13.2	
30.00	5.39	6.1	84.44	15.3	
48.50	11.03	11.4	48.40	19.5	
51.00	11.88	11.4	48.6	19.2	
			55.99	22.4	
			60.00	23.4	

	K ₄ FeC ₆ N ₆ .	1	CO(NH ₂) ₂ .	
14.	X.	n.	X.	
3.70	10.5	50	3.4	
5.95	19.9	50	8.6	
5.99	19.9	25	0.4	
7.32	25.0	25	0.6	
10-9	42.1	 }		

TABLE XI.—continued.

VIII. Discussion of Results.

14.50

15.11

66.7

69.8

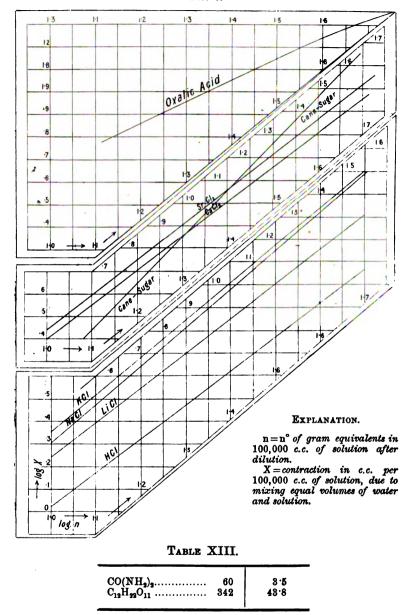
Methods of Formulating the Results.—Several methods of representing the results were attempted, and at first it seemed probable that an equation of the form $X = An + Bn^2$ would be satisfactory, but as greater accuracy was attained it became clear that the deviation from this equation was systematic and greater than the error of observation. Finally, the equation $X = n^b/a$ was used, and in most cases gives values of X agreeing well with observation. In the case of oxalic acid and potassium ferrocyanide, this equation does not, however, seem to express the results. The comparison of the values of X calculated from the equation with those actually observed is made in Tables X and XI, and Fig. 3 (p. 272) shows curves drawn from the equation. The logarithms are plotted, not the actual values of X and n.

Relation of Contraction to Equivalent Weight.—If the contractions due to diluting the various substances examined are written down in order of magnitude, they will be found to stand in the same order as the equivalent weights of the substances. This is shown in Tables XII and XIII, which contain the results for electrolytes and non-electrolytes respectively.

TABLE XII.

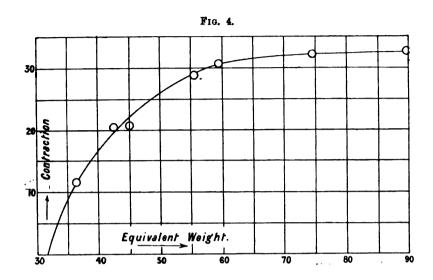
Name and equivalent weight of dissolved substance.	Contraction due to diluting from normal to half-normal.
HCl 86·5	11.5
LiCl 42.5	20.2
LC.H.O. 45	20.8
½C₂H₂O₄ 45 ½CaCl₂ 55·5	28.8
™aCl 58·5	80.9
KCl 74.5	32.2
4SrCl, 89.5	32.8
K.FeC.N. 92.0	51.0

Fig. 3.



The curve, Fig. 4, shows the contraction as a function of the equivalent weight; electrolytes alone are considered, and with the exception

of potassium ferrocyanide the relation seems well marked. Nonelectrolytes evidently contract very much less, other things being equal, than electrolytes, but there are not sufficient data as yet to construct a curve.



Contraction Regarded as Change in the Volume of Dissolved Substance.

Perhaps the most interesting way to look at the contractions is to consider them as changes in the apparent volume of the dissolved substance. For if the observed contraction is divided by n, the quotient is the change in the apparent volume of 1 gram equivalent of dissolved substance in undergoing 50 per cent. dilution. This is expressed in the equation

$$\phi_{2n} - \phi_n = X/n = n^{b-1}/a,$$

where ϕ_{2n} , ϕ_n are the apparent volumes of 1 gram equivalent of dissolved substance before and after the 50 per cent. dilution, n the number of gram equivalents per 100,000 after dilution (and, therefore, 2n the number before). The solution of this equation is

$$\phi_n = \text{const.} + \frac{n^{b-1}}{a(2^{b-1}1)}$$

where a, b are known from the tables given on pp. 269, 270. The remaining constant can be found from one accurate determination of the density, and where such a determination has been placed on

record it is possible to make complete tables of ϕ at various strengths.

Table XIV gives such values of ϕ .

TABLE XIV.

Substance NaCl. Temperature 18°.

I,	II.	III.	IV.
n.	φ-const.	Const. assumed.	φ.
10	0·3211	16:361	16.68(2)
20	0·5214		16.88(2)
30	0.6944		17·05(5)
40	0.8470		17·20(8)
50	0.9902		17·35(1)
75	1.3153		17·67(6)
100	1.6090		17.97(0) *

^{*} This number is based on an observation by Gerlach.

Substance SrCl₂. Temperature 18:0°.

10	0.6066	10.852	11.45(9)
20	0.8819		11.78(4)
80	1.0975		11.95(0)
40	1.2820		12.13(4)
50	1.4449	1	12.29(7)
75	1.7983		12.65(0)
100	2.1029	1	12.95(5)
65.8	1.6775		12.58*

^{*} This number is based on an observation by Kohlrausch.

Substance CaCl₂. Temperature 18°.

10	0.5749	10.149	10.72(4)
20	0.8244		10.97(8)
80	1.0179		11.16(7)
40	1.1823	1	11.33(1)
50	1.3275	ŀ	11.47(7)
75	1.6390		11.78(8)
100	1.9038		12.05(3)
98.8		İ	11.99(0) *

^{*} This number is based on an observation by Kohlrausch.

TABLE XIV.—continued. Substance HCl. Temperature 18°.

I.	II.	III.	IV.
n,	φ-const.	Const. assumed.	φ.
10 20	0·2595 0·3648	17:819	18:07(9)
80	0.4443	•	18·18(3) 18·26(3)
40	0.5118		18.33(1)
50	0.5708		18 ·3 9(0)
75	0.6962		18.51(5)
100	0.8013		18·62(0) ¹

^{*} Based on an observation by Kohlrausch.

Substance C₁₂H₂₂O₁₁. Temperature 18°.

	1		!
10	0.175	209.750	209.92(5)
20	0.350		210.10(0)
80	0.525	i .	210.27(5)
40	0.700	1	210.45(0)
50	0.875	i	210.62(5)
75	1.312	1	211.06(2)
100	1.750	Ĭ	211.50(0) *
=	= 100		=== 55(5)

^{*} Based on an observation by Gerlach.

Substance KCl. Temperature 20°.

10	0.4094	26.685	27.09(4)
20	0.6380	}	27.32(3)
30	0.8272		27.51(2)
40	0.9941	ŀ	27.67(9)
50	1.1468	1	27.83(2)
75	1.4860		28.17(1)
100	1.7870		28.47(2)
107.7	1.8745	1	28.56(0)

^{*} Based on an observation by Nicol.

Substance LiCl. Temperature 18°.

0.8956	18:408	18.80(4)
0.5662		18.97(4)
0.7078		19.11(6)
0.8246		19.23(3)
0.9280	1	19.82(8)
1.1508		19.55(9)
1.3400		19.74(8)
1.4821		19.89(0) *
	0.5662 0.7078 0.8246 0.9280 1.1508	0 5662 0 7078 0 8246 0 9280 1 1508 1 3400

^{*} Based on an observation by Kohlransch. by Google

The curves (Fig. 5) exhibit the values of ϕ . It should be remembered that the author is only directly responsible for the *changes* in ϕ , and that the absolute values are affected by errors, if any, in the "constant assumed" which is dependent on the accuracy of existing density determinations.

The values of ϕ are given partly in the hope that they will prove of practical value in physico-chemical work. In many branches of physical chemistry, solutions are prepared by dilution of stock solutions, and the experimenter wishes to know the concentration of the solution obtained, in, say, gram molecules per 100 grams of water. A continuous table of molecular volumes affords the easiest method of arriving at the result. Partly, again, because the values of X only tell us the volume change on 50 per cent. dilution, whereas the tables of ϕ gives us continuous information of the change of volume due to any given dilution. In the diagram, Fig. 5, ϕ is shown as a function of n for various substances. As, however, it would be impossible to depict the various curves on the same page without greatly diminishing the scale, it has been necessary to subtract a constant round number from the values of ϕ before These numbers are, for LiCl, 18; NaCl, 16; KCl, 27; HCl, 18; CaCl, 10; SrCl, 11; Cane sugar, 209.

Conclusion.

The following empirical laws have been arrived at by the experiments described.

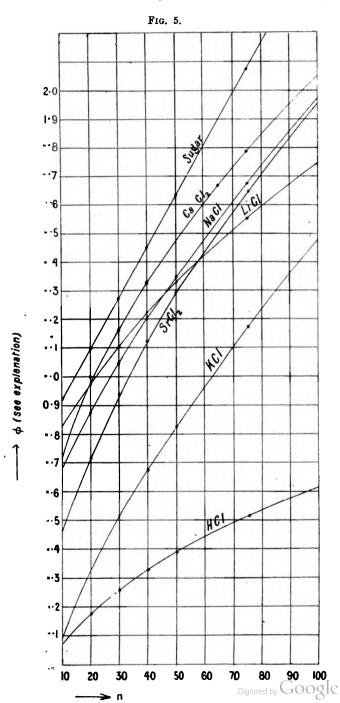
1. X (as defined on p. 268, Table IX) is in almost all cases given by the following equation, $X = n^b/a$, and, consequently, ϕ (as defined, p. 273) must be given by

$$\phi = \text{const.} + \frac{n^{b-1}}{a(2^{b-1}1)}$$

2. For comparable substances and concentrations, X increases with the equivalent weight of the substance in a regular way.

It is hoped that these empirical rules, together with the tables of contraction and of molecular volumes, will be sufficient excuse for the publication of this paper. It should be added that the apparatus described is applicable without modification to many other physicochemical problems, such as change of volume on neutralisation, change of volume on mixing two different liquids (for example, alcohol and water), changes of volume on formation of double salts in solution. The author hopes to proceed with the study of volume changes on neutralisation of organic acids without delay.

The writer's best thanks are due to Prof. J. J. Thomson for permission to work in the Cavendish Laboratory, and to Mr. Griffiths and Mr. Whetham for the interest taken in the work throughout.



XXIX.—Methanetrisulphonic Acid.

By ERNEST HAROLD BAGNALL, B.Sc.

THE sulphonic acids of methane, the simplest hydrocarbon, are substances of more than ordinary interest, and, although the mono-, diand tri-sulphonic acids, $CH_s \cdot HSO_s$, $CH_2(HSO_s)_2$, and $CH(HSO_s)_3$, have long been known, no work on them has been published during the last five-and-twenty or thirty years.

Of these, methanetrisulphonic acid, CH(HSO₃)₃, the subject of this paper, was discovered by Theilkuhl (*Annalen*, 1868, 147, 134), and subsequently examined by Rathke (*ibid.*, 1873, 167, 219).

In attempting to prepare the various sulphonic acids and sulphones of dichlorobenzidine by the action of fuming sulphuric acid on dichlorodiacetylbenzidine, a substance was obtained which, on analysis, was found to be methanetrisulphonic acid; as it can be easily prepared by the methods described in this paper, I have carefully examined the acid, and also studied the properties of its various salts.

Preliminary experiments soon showed that the formation of methanetrisulphonic acid was really due to the presence of the acetyl groups in dichlorodiacetylbenzidine, as diacetylbenzidine under similar treatment gave a large quantity of the acid, whereas benzidine sulphate gave only benzidinesulphone and the various sulphonic acids of benzidine (Ber., 21, Ref., 873; 22, 2467). Similarly, acetyl-a-naphthylamine gave a small quantity of methanetrisulphonic acid.

As this reaction appeared to be a general one for the acetyl derivatives of benzidine and naphthylamine, it was anticipated that the acetyl derivative of aniline and the anilides of the higher fatty acids would yield methanetrisulphonic acid, or its homologues, as one of the products, and this was found to be so in the case of acetanilide. Acetanilide, when heated with fuming sulphuric acid, gives a remarkably good yield of methanetrisulphonic acid, along with anilinedisulphonic acid, NH₂·C₆H₃(HSO₃)₂ [1:2:4]. Other anilides were experimented with, but the results were not satisfactory; the anilide of propionic acid gave a very small quantity of methanetrisulphonic acid, but neither ethanedisulphonic acid nor sulphopropionic acid could be detected (compare Buckton and Hofmann, J. Chem. Soc., 1856, 9, p. 241).

It is difficult to understand the general nature of these reactions. Much sulphurous anhydride and carbonic anhydride are always evolved, and it seems probable that some of the organic substance is oxidised to carbonic anhydride, and some converted into aromatic sulphonic acids,

the acetyl group alone reacting with the fuming sulphuric acid to form methanetrisulphonic acid. Glacial acetic acid, however, when heated with fuming sulphuric acid, gives no methanetrisulphonic acid; the sulphur trioxide dissolves in the acetic acid without giving off gas, and sulphacetic acid, $CH_2(HSO_3) \cdot COOH$, is formed. It was anticipated that, on heating acetamide with a large excess of fuming sulphuric acid, methanetrisulphonic acid would also be produced, but this is not the case; the product consists entirely of methanedisulphonic acid, $CH_2(HSO_3)_2$, which was first isolated by Liebig (Annalen, 1835, 13, 35), and subsequently prepared and examined by Wetherill (ibid., 1850, 66, 122), Strecker (ibid., 1856, 100, 199), and by Buckton and Hofmann (J. Chem. Soc., 1856, 9, 241), and Rathke (Annalen, 1873, 161, 152).

EXPERIMENTAL.

Preparation of Methanetrisulphonic Acid.

Action of Fuming Sulphuric Acid on Dichlorodiacetylbenzidine .-As stated in the introduction, it was from this substance I first obtained methanetrisulphonic acid. Dry powdered dichlorodiacetylbenzidine (16.85 grams) was heated on a water-bath at 100° with fuming sulphuric acid (100 grams, containing 70 per cent. free SO₂), mixed with pure sulphuric acid (100 grams) until the whole dissolved.* The mixture was then heated for 3 hours on a sand-bath at a temperature of 150°, with constant stirring, and left overnight. poured on to ice, filtered to remove a dirty green precipitate which probably contains the sulphones and sulphonic acids of dichlorobenzidine, and the dark brown filtrate neutralised with milk of lime, heated to boiling, and rapidly filtered from the precipitated calcium sulphate. To the clear filtrate, evaporated to a small bulk, sodium carbonate solution was added in quantity just sufficient to precipitate all the calcium as carbonate. This was filtered off, and the filtrate concentrated and allowed to cool slowly, when it deposited yellow crystals; these were collected, dissolved in a small quantity of water, and glacial acetic acid added; the white, crystalline precipitate of the sodium salt of methanetrisulphonic acid, CH(NaSO₈)₈ + 3H₂O, thus obtained, was analysed.

* Great care is required in the mixing of fuming sulphuric acid with concentrated sulphuric acid; to prevent accident, the concentrated sulphuric acid should be poured into the fuming acid, not *vice versa*.

It is better to carry out these anlphonations in a porcelain beaker, the mouth of which is covered with a close-fitting clock-glass. A hole is bored through the centre of the clock-glass, so as to admit a glass stirring rod which is connected with a water-motor. With this arrangement, very little sulphuric anhydride escapes into the air.

This salt crystallises in six-sided plates, with $3 \rm{H}_2 \rm{O}$, easily soluble in water, and is not, therefore, as suitable as the potassium salt for isolating methanetrisulphonic acid from an aqueous solution. On heating the anhydrous sodium salt in a tube, sulphur sublimes and sulphurous anhydride is evolved, together with a little hydrogen sulphide and carbon bisulphide; the residue consists almost entirely of sodium sulphate. It is remarkable that when glacial acetic acid is added to an aqueous solution of sodium methanetrisulphonate, the salt is precipitated almost completely in crystals.

Action of Fuming Sulphuric Acid on Diacetylbenzidine.—In this experiment, 100 grams of fuming sulphuric acid containing 70 per cent. free SO₃, 50 grams of concentrated sulphuric acid, and 20 grams of dry, powdered diacetylbenzidine were used, the operation being carried out exactly as in the first case, with the exception that the calcium salt was decomposed with potassium carbonate; the potassium salt thus obtained is much less soluble in water than the sodium salt, and, therefore, more suitable for the isolation of the acid. The yield of potassium methanetrisulphonate obtained is very good, the above quantities yielding about 35 grams of the pure salt.

Action of Fuming Sulphuric Acid on Acetyl-a-naphthylamine.—One hundred grams of dry, powdered acetyl-a-naphthylamine, prepared in the usual way, was heated with 100 grams of fuming sulphuric acid (70 per cent. SO₃) and 50 grams of concentrated sulphuric acid, as in the other cases. The yield of methanetrisulphonic acid produced in this way is but poor, considerable quantities of ammonium sulphate being formed during the reaction.

Action of Fuming Sulphuric Acid on Acetanilide.—As this method gives the best yield of methanetrisulphonic acid, it is described in detail. Five grams of dry, powdered acetanilide were slowly added to a mixture of 30 grams of fuming sulphuric acid (70 per cent. free SO₃) and 15 grams of pure concentrated sulphuric acid, the mixture being constantly stirred and heated at 130° for three hours. The ambercoloured, viscous product, when cold, was poured into water, boiled, and neutralised with milk of lime; not a trace of aniline was li berated. The liquid was filtered hot, and sufficient potassium carbonate solution added to the filtrate to convert the soluble calcium salts

into the potassium salts. The filtrate from the calcium carbonate, when concentrated and left to cool, deposited beautiful, colourless prisms of almost pure potassium methanetrisulphonate. These were collected, drained on a porous plate, and recrystallised from boiling water. On analysis, they gave the following results.

This potassium salt loses its water of crystallisation at 210°, and when heated in a tube behaves like the sodium salt. It is insoluble in absolute alcohol, ether, and glacial acetic acid, and is only sparingly soluble in cold water, 1 part requiring 89 parts at 18° for solution; it dissolves readily in hot water, from which it is again deposited, on slowly cooling, in beautiful, colourless prisms often over an inch in length. Phosphorus pentachloride has no action on the anhydrous salt. As in the case of the sodium salt, glacial acetic acid precipitates the potassium salt and all the other salts of methanetrisulphonic acid, unchanged from their aqueous solutions.

To trace the part the aniline took in the action of fuming sulphuric acid on acetanilide, the mother liquor from the first crop of crystals of potassium methanetrisulphonate was further concentrated and placed on one side to cool, when a second crop of crystals of the trisulphonate was obtained; these were filtered off and the filtrate fractionally precipitated by glacial acetic acid. The precipitate, first formed on adding glacial acetic acid, was rejected as retaining generally traces of potassium methanetrisulphonate. The further addition of glacial acetic acid to the filtrate produced a white, silky precipitate of the hydrogen potassium salt of anilinedisulphonic acid,

 $NH_2 \cdot C_6H_8(KSO_3) \cdot HSO_3 [1:2:4],$

first prepared by Buckton and Hofmann (loc. cit.) by the action of fuming sulphuric acid on aniline. The anhydrous salt gave the following results on analysis.

```
0.3318 gave 0.3042 CO<sub>2</sub> and 0.0662 H<sub>2</sub>O. C = 25.00; H = 2.20. 0.1807 , 0.0541 K<sub>2</sub>SO<sub>4</sub>. K = 13.43.
```

0.2815 , 0.4410 BaSO₄. S = 21.51.

0.3151 ... 13 c.c. nitrogen at 775.2 mm. and 20°. N = 4.92.

 $NH_2 \cdot C_6H_3(KSO_3) \cdot HSO_3$ requires C = 24.74; H = 2.06; S = 21.99; K = 13.40; N = 4.81.

To further identify this substance, it was dissolved in water and

treated with bromine water; the yellow precipitate produced sublimed in beautiful, colourless needles which melted at 137°, and gave, on analysis, numbers corresponding with the formula of β -tribromaniline $C_6H_2Br_8\cdot NH_2$ [1:2:4:5]. The production of the acid potassium salt of anilinedisulphonic acid in the above reaction is due to the fact that glacial acetic acid, when added to an aqueous solution of the neutral potassium salt of anilinedisulphonic acid, throws down the acid potassium salt, which is much less soluble in water than the neutral salt.

Action of Fuming Sulphuric Acid on Propanilide.—Thirty grams of pure, powdered propanilide were added in small quantities to a mixture of 110 grams of fuming sulphuric acid (70 per cent. SO₂) and 50 grams of concentrated sulphuric acid, and the whole heated at 110° for two hours; on cooling, the product was poured into water, and, curiously enough, ethylic alcohol was given off. The solution was treated as in the other cases, first with milk of lime, and subsequently with a solution of potassium carbonate; in this way, a substance was obtained which, after recrystallisation from dilute acetic acid, gave numbers, on analysis. showing it to be the hydrogen potassium salt of anilinedisulphonic acid, $NH_{\circ} \cdot C_{\circ}H_{\circ}(KSO_{\circ}) \cdot HSO_{\circ}$ [1:2:4]. By this method, anilinedisulphonic acid alone is isolated; to obtain what little methanetrisulphonic acid is formed, the product was poured into water, neutralised with calcium carbonate, filtered, and the filtrate treated with excess of a solution of ammonium carbonate; it was then again filtered, boiled with barium carbonate, and filtered while hot. On cooling, a small quantity of a crystalline barium salt separated which showed all the characteristic properties of barium methanetrisulphonate. The salt, dried at 180°, was analysed.

0.1117 gave 0.0844 BaSO₄. Ba = 44.43. Ba₃[CH(SO₃)₃]₂ requires Ba = 44.82 per cent.

What part the propionic radicle takes in this reaction it is not easy to say; certainly a large quantity of the acid escapes during the reaction as free propionic acid, and furthermore, as just state, ethylic alcohol is also produced, which must have come from this source. Neither ethanedisulphonic acid nor sulphopropionic acid could be detected.

Methanetrisulphonic Acid and its Salts.

Methanetrisulphonic Acid.—In preparing this acid, the pure barium salt was suspended in warm water and cautiously decomposed with pure sulphuric acid, a slight excess of the acid being used; after heating on the water-bath for a few hours, the liquid was filtered from barium sulphate and evaporated; the syrupy residue, when kept for 2 or 3 days

in a good vacuum over sulphuric acid, deposited beautiful, colourless needles. The crystals, after draining on a porous plate in a vacuum, gave the following numbers on analysis, very accurate results being difficult to obtain as the acid is exceedingly hygroscopic.

- I. 0.6741 gave 0.0750 CO₂ and 0.2001 H₂O. C = 3.03; H = 3.29.
- II. 0.5480 , 0.0557 CO_2 , $0.1636 \text{ H}_2\text{O}$. C = 2.77 ; H = 3.31. 0.2720 , 0.6025 BaSO_4 ; S = 30.42.
- CH(HSO₃)₈ requires C = 4.68; H = 1.56; S = 37.50 per cent. CH(HSO₃)₈ + $4H_2$ O requires C = 3.65; H = 3.65; S = 29.26 per cent.

This analysis appears to show that the acid has probably the formula $CH(HSO_8)_8 + 4H_2O$. Unfortunately, it is not possible to estimate the water of crystallisation by the ordinary method, as the acid decomposes at 180° before all its water of crystallisation has been given off.

Methanetrisulphonic acid melts between 150° and 153°, and dissolves very easily in water with development of heat; it is very deliquescent, has a pure acid taste, and turns blue litmus red. It is not changed, and no sulphuric acid is produced by boiling it with nitric acid, or when chlorine gas is passed through an aqueous solution of the The salts of methanetrisulphonic acid are readily obtained by digesting the carbonates of the various metals with an aqueous solution of the acid. The barium salt is precipitated as a white, sparingly soluble, crystalline precipitate on adding barium chloride to an aqueous solution of the acid. The other salts are all more or less soluble in water, but insoluble in alcohol, and in glacial acetic acid. Phosphorus pentachloride has no action on it in the cold, but on slightly warming decomposition takes place; it was not possible, however, to isolate the product in a pure state. Methanetrisulphonic acid immediately unites with aniline with evolution of heat, forming the aniline salt, CH(HSO₃)₃(C₆H₅·NH₂)₃.

Silver Methanetrisulphonate, $\mathrm{CH}(\mathrm{AgSO_3})_3 + \mathrm{H_2O}$.—To prepare this salt, freshly prepared silver carbonate was added to a solution of the pure acid until the liquid was neutral, and the filtrate concentrated on a water-bath and allowed to cool, when slender crystals of the silver salt gradually separated. The salt crystallises with $1\mathrm{H_2O}$, which it loses at 180° , but if it is heated above 180° , it darkens and begins to decompose. Silver methanetrisulphonate is soluble in water, but insoluble in absolute alcohol.

```
2.3512 lost 0.0748 H_2O at 180°. H_2O = 3.18.
```

1·2126 (anhydrous salt) gave 0·0915 CO_2 and 0·1950 H_2O . C = 2·05; H = 0·17.

0.5477 (anhydrous salt) gave 0.3070 Ag. Ag = 56.03.

0.4298 ,, ,, 0.5104 BaSO_4 . S = 16.30.

 $CH(SO_3Ag)_3$ requires C = 2.07; H = 0.17; Ag = 56.13; S = 16.63 percent. $CH(AgSO_3)_3 + H_2O$ requires $H_2O = 3.02$ per cent.

To determine the sulphur in the silver salt, Carius' method was first tried, but, as in the case of the calcium and barium salts, the silver salt crystallised out of the nitric acid quite unchanged at the end of the process, even after heating at a temperature of 210° ; this is remarkable, as most silver salts of organic acids are decomposed by nitric acid under these conditions. The sulphur is easily determined, however, by fusing the salt with pure potassium nitrate and carbonate.

It was anticipated that the ethylic salt of methanetrisulphonic acid would be formed by heating silver methanetrisulphonate with ethylic iodide, and in order to investigate this point, 4 grams of the anhydrous silver salt were mixed, in a dry flask, with 6 grams of ethylic iodide dissolved in absolutely dry ether, and the mixture heated in a reflux apparatus for 6 hours; on extracting with ether and removing the ether by evaporation, no residue was left, and most of the silver salt was recovered unchanged.

Barium Methanetrisulphonate, $\mathrm{Ba_3[CH(SO_3)_3]_2} + 9\mathrm{H_2O}$.—When a solution of barium chloride is added to a solution of methanetrisulphonic acid or any of its salts, a most characteristic behaviour is noticed, and this may be used for detecting the presence of methanetrisulphonic acid; on mixing the two solutions, nothing takes place for a few moments, and then, suddenly, a crystalline precipitate of the barium salt separates. The crystals were collected, well washed, and analysed.

 $\begin{array}{lll} 0.2189 \ (anhydrous \ salt) \ gave \ 0.1660 \ BaSO_4. & Ba=44.58. \\ 0.5340 \ gave, \ at \ 220^\circ, \ 0.0810 \ H_2O. & H_2O=15.16. \\ Ba_3[CH(SO_8)_8]_2 \ \ requires \ Ba=44.82 \ \ and \ Ba_3[CH(SO_3)_8]_2 + 9H_2O \ \ requires \ H_2O=15.01 \ \ per \ cent. \end{array}$

Barium methanetrisulphonate dissolves very sparingly in boiling water, and crystallises on cooling either in the form of leaflets or needles, the temperature and concentration of the solution evidently determining the crystalline form. Strong nitric acid even under pressure does not decompose the barium salt, and the salt crystallises unchanged from 50 per cent. hydrochloric acid.

Calcium Methanstrisulphonate, Ca₈[CH(SO₃)₃]₂ +12H₂O.—This salt crystallises with 12H₂O in very small prisms which become anhydrous at 180°. It is very soluble in water, less soluble in dilute alcohol, and insoluble in absolute alcohol or glacial acetic acid, and remains unchanged when heated under pressure with nitric acid and potassium dichromate.

Copper Methanetrisulphonate, $Cu_3[CH(SO_3)_3]_2 + 12H_2O$.—This salt is obtained on decomposing barium methanetrisulphonate, suspended in boiling water, with the requisite quantity of a solution of copper sulphate, and the filtrate from the barium sulphate, after concentration on a water-bath, is left overnight over sulphuric acid in a

vacuum; prismatic needles of the copper salt gradually separate, and these, after draining on a porous plate, were analysed.

1.2784 lost 0.3010 H_2O at 160°. $H_2O = 23.51$.

0.2954 .. 0.0780 CuO. Cu = 21.06.

 $Cu_{s}[CH(SO_{s})_{s}]_{o} + 12H_{o}O$ requires $H_{o}O = 23.71$; Cu = 20.74 per cent.

Ammonium Methanetrisulphonate, CH(NH₄SO₃)₃.—This was prepared by neutralising an aqueous solution of the pure acid with ammonia, and exposing the solution in a vacuum over sulphuric acid, when crystals of the salt separated.

0.2995 gave 0.0493 NH₈. NH₈ = 16.46. CH(NH₄SO₈)₈ requires NH₈ = 16.61 per cent.

Ammonium methanetrisulphonate appears to crystallise in stumpy prisms or plates, probably belonging to the monosymmetric system. This research was carried out in the laboratories of the Owens College, Manchester, at the suggestion of Professor Perkin.

CRYSTALLOGRAPHICAL.

For the accompanying measurements of silver methanetrisulphonate, and description of the crystallographical character of the other salts of methanetrisulphonic acid, I am indebted to Mr. W. J. Pope.

Silver Methanetrisulphonats.—This crystallises in small, white, opalescent, iridiscent plates belonging to the orthorhombic system; the crystals are somewhat irregularly developed, and the faces in the zone [100:010] are deeply striated with lines parallel to the c axis. The extinction in $a\{100\}$ is parallel to the edge ap, and the acute bisectrix emerges normally to a(100); the optic axial plane is c(001), the optic axial angle is large, and the double refraction is negative in sign and weak.

Crystalline system.—Orthorhombic.

a:b:c:=2.9152:1:0.5422.

Forms present $a \{100\}$, $b \{010\}$, $p \{110\}$, $q \{011\}$ and $q' \{012\}$.

The following angular measurements were obtained.

Angle.	Number of measurements.	Limits.	Observed.	Calculated.		
ap = 100:110 $bp = 010:110$ $pp = 110: 110$ $pp = 110: 110$ $pp = 10: 011$ $pq = 010: 011$ $pq = 011: 011$ $pq' = 011: 012$ $pq' = 012: 012$	17 39 24 20 32 24 11 16	18°22′— 19° 3′ 70 45 — 71 26 141 48 —142 80 37 81 — 38 11 61 18 — 61 52 56 81 — 57 28 13 1 — 18 26 30 14 — 30 39	18°49' 71 4 142 9 37 46 61 32 56 59 13 14 30 26	18°56′		

Barium Salt.—The crystals consist of minute, rhomboidal shaped plates, the acute angle being 76°; the extinction bisects the angles of the rhomb.

Sodium Salt.—The crystals consist of long, six-sided plates, in which the extinction is parallel to one pair of edges; the large face is perpendicular to the positive bisectrix of a large optic axial angle.

Potassium Salt.—The crystals consist of large, monosymmetric prisms, showing the forms {100}, {001}, {110}, and {111}. The optic axial plane is perpendicular to the plane of symmetry, and one optic axis emerges nearly normally through the face (110).

XXX.—Maltodextrin: its Oxidation-Products and Constitution.

By Horace T. Brown, LL.D., F.R.S., and J. H. MILLAR.

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I. Introduction.

In a paper published thirteen years ago by one of us and G. H. Morris (Trans., 47, 1885, 527), a substance was described under the name of maltodextrin,* which had been isolated from a mixture of

^{*} The term maltodextrin is due in the first instance to Herzfeld, who, as far back as 1879, employed it to describe a derivative of starch which, in many respects, although not in all, corresponded with the subject of this paper (see Herzfeld, Inaug. Diss. Halle, 1879; also Ber., 1885, 18, 3469; ibid., 1886, 19, 483). More recently, Armstrong suggested the term amyloin as being generally applicable to substances of this class. Both terms are convenient, since they recall the fact that the substances in question, of which probably a series exists, may be regarded as combinations of amylin or dextrin groups, with amylon or maltose groups.

the products obtained by the restricted hydrolysis of starch by malt diastase.

This was a non-crystallisable substance, having definite optical and reducing properties corresponding to $[a]_{rss}$ 193·1°, and κ_{rss} 21·1. Expressed in the notation now usually adopted, these values are equivalent to $[a]_D$ 180°. R 34·5, the reducing power of maltose being R 100.

The homogeneity of maltodextrin was proved by the persistence of the above optical and reducing powers under continued fractionation with alcohol, and also by the fact that it would pass slowly through a dialyser without change. Its unfermentability with ordinary yeast, and the subsequently ascertained fact that it yields no crystallisable osazone with phenylhydrazine, proved the absence of ordinary maltose from maltodextrin.

One of the most marked characteristics of maltodextrin, and of the amyloins generally, was found to be the complete conversion into crystallisable and fermentable maltose under the action of the very active diastase of air-dried malt; it was not converted into a definite mixture of maltose and a comparatively stable dextrin in the same way that soluble starch is under similar conditions.

In the paper of 1885 above cited, it was considered that the facts known up to that time warranted the conclusion that the formula of maltodextrin might be written as $\begin{cases} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{cases}; \text{ that is, as a combination of two amylin or dextrin groups with one amylon or maltose group.}$

Subsequent determinations of the molecular weight by the freezing point method appeared to confirm this view, but we do not lay much stress on this fact, since we are now convinced that the method of freezing is not by any means generally applicable to the non-crystal-lisable products of starch-hydrolysis.

The present paper, together with the communications immediately following it, give an account of the principal results we have obtained during the past two years of continuous work on the subject of starch-hydrolysis. The latter part of the research has been carried on in the Davy-Faraday Research Laboratory of the Royal Institution, and we take this opportunity of tendering our thanks to the Directors and to Dr. A. Scott for the facilities they have given us.

The methods hitherto employed for the separation and examination of the starch products have necessarily been very limited, and have for the most part been confined to (1) a determination of the optical and reducing constants of the products after as complete a separation as possible by alcoholic fractionation; (2) an inquiry into the mode of

action of diastase on the separate substances; and (3) their behaviour with phenylhydrazine. Occasionally, attempts have been made to determine the molecular weight by the freezing point method, and sometimes also the action of yeast has been tried, with or without the addition of diastase.

These methods, which are necessarily very imperfect, have often given different results in the hands of different experimenters; indeed, so far is this the case that there may be said to be no unanimity even as regards the main facts of starch-hydrolysis.

After turning our attention to the improvement of the existing methods of analysis of starch products, the results of which we laid before the Society in 1897 (Trans., 1897, 71, 72, 109, 115, 275), we endeavoured to supplement the older methods of attack with others.

The one, which up to the present has been by far the most promising, is based on a study of certain well-defined oxidation products which can be obtained from some of the non-crystallisable starch derivatives. These are complex carboxylic acids which are capable of further hydrolysis by diastase and dilute acids respectively. An examination of the salts of these acids, and a determination of the exact amount of sugars which they yield on hydrolysis, has thrown much light on the constitution of the polysaccharide before oxidation, and the method appears to be capable of considerable extension. In the present paper, we shall confine ourselves to the study of the acid derivatives of maltodextrin.

II. Preparation of Maltodextrin.

The preparation of maltodextrin in a state of purity, and in sufficient quantity to admit of satisfactory work, is, in itself, a difficult matter. It must be remembered that we have to deal with an absolutely uncrystallisable substance, differing only very slightly in solubility from various other colloidal substances of a somewhat similar nature always accompanying it in the mixture of partially hydrolysed starch products from which it has to be separated; it is only by long and very laborious fractionation with alcohol that the required result can be attained. If we commence with the mixed products derived from 2000—2500 grams of starch, we may consider ourselves fortunate if we can obtain 350—370 grams of crude maltodextrin, and this will probably be reduced to from 50 to 60 grams by the time it is sufficiently purified. Such a fractionation generally requires from two to three months to be effectually carried out.

The modus operandi which we have found to answer the best is as follows.

About 2 kilos. of well-washed potato starch are used in each opera-

tion. Such an amount of starch, by the ordinary process of gelatinisation, which must, of course, precede hydrolysis, would require as much as 50 litres of water, since a starch-paste of much more than 4 per cent. concentration becomes unmanageable.

In order to reduce the volume of liquid to a reasonable point, so as to obtain the products of hydrolysis in a fairly concentrated state, the following device was adopted. Five hundred grams of the starch, that is, one-quarter of the whole amount, were gelatinised with 12 litres of water at 100° in the ordinary manner; the starch-paste so obtained was then cooled to about 60°, and to this a trace of malt extract was added, just sufficient to destroy its viscidity. The solution was once more heated to 100° and made use of for gelatinising a further quantity of the starch, which was in turn rendered just liquid with malt extract after, of course, cooling to 60°. These operations were repeated until the whole of the 2000 grams of starch were obtained in solution in from 12 to 13 litres of liquid. This was finally hydrolysed to the required extent with an amount of finely divided malt equal in amount to about 2 per cent. by weight of the starch employed.*

It is better to take a kiln-dried rather than an air-dried malt for this purpose, so as to ensure the limitation of the diastatic action. We prefer a malt with a diastatic power of about 38 according to Lintner's standard. The temperature of the transformation should be 65°, and the progress of the reaction must be followed with the polariscope, and arrested by boiling when the specific rotatory power has fallen to about $\lceil \alpha \rceil_0$ 168° to \uparrow 175°.

In some cases, the filtered solution, containing about 15 per cent. of mixed starch products, was submitted to fermentation for a few days with a little washed yeast, so as to remove the greater part of the maltose, but, on the whole, we prefer to separate the maltose by alcoholic fractionation only.

The solution of mixed products, after evaporation to a thin syrup, is then poured into about 5 litres of alcohol of 90 per cent. (by volume), which is reduced to about 87 per cent. by the water of the syrup, and the mixture is digested on a water-bath for some hours at

* We have sometimes employed about 40 c.c. of a cold-water malt-extract instead of malt. This is made by digesting finely divided malt with 2½ times its weight of cold water for 6 to 8 hours. The filtered liquid must be heated to 65° for about 15 minutes before it is used, so as to restrict the diastatic power. If this latter precaution is not taken, there is danger of running the hydrolytic process down too far, thus reducing the yield of maltodextrin.

† In the previous paper of 1885 on maltodextrin, it was recommended to commence with a transformation whose united products has a specific rotatory power of about [a] 180. We have since found that the lower value mentioned in the paper gives the best yield of maltodextrin.

the boiling point of the alcohol, with frequent agitation; it is then allowed to cool slowly, and the clear alcoholic liquid poured off and distilled. The residue from the first digestion is now treated in a similar manner with successive quantities of 3 litres of alcohol of a uniform strength of 85 per cent., each digestion being continued for a whole day. In this manner, the original starch products are split up into 15 or 20 principal fractions, the early members of which contain most of the maltose, and have a lower specific rotatory power than the later fractions. It is the intermediate and later fractions which contain most of the maltodextrin, whilst the greater part of the 'stable' dextrin is left in the residue insoluble in 85 per cent. spirit.

The first three or four of the principal fractions are rejected entirely, and the remainder, selected according to their specific rotatory power, are re-united to form two more parent fractions for subsequent treatment, one of them, A, being made up of fractions with an $[a]_D$ of from about $164-173^\circ$, and the other, B, of all the remaining fractions possessing a specific rotatory power lying between about $[a]_D$ 174° and 182° .

Fraction B, which may amount in such an experiment to 350 or 400 grams, consists for the most part of a mixture of various maltodextrins with a little maltose which is detectable with phenylhydrazine. When treated with a little malt-extract (from air-dried malt) at 50° for an hour, it yields about 94 per cent. of maltose, so that the amount of stable dextrin in the mixture must be very small.

Both A and B are further fractionated in an exactly similar manner, but using alcohol of 90 instead of 85 per cent. Selections from the resulting fractions are again made according to optical activity and reducing power, and those are again united whose properties approach the maltodextrin sought, a similar process of treatment being continued until a product is obtained which is no longer capable of being further differentiated by alcohol.

Such a procedure necessarily occupies a very long time, and the constant elimination of the less pure products results in a very small final yield of maltodextrin.

We here give, in diagrammatic form, an example of one of many such fractionations which we have made during the progress of our work. In this particular case, which was not exceptional in any way, the complete separation occupied nearly three months, and entailed about sixty separations.

Table of Fractionations of Maltodextrin.

CONVERSION

Residue. 86 per cent. alcohol by fermentation. 17. 188·3 38·7 염! Starch, 2000 grams. [a]D 183:1 R 29:8 15. 11 61 CONVERSION II. انم 90 per cent. alcohol. 13 ١نم [a]b 12. 179·3 85 per cent. alcohol 88 per cent. alcohol. 5. 6. 7. 188:51188:01187:4 41:5 39:9 37:8 Fractions marked × mixed 90 per cent. alcohol. [a]o 184·5. R 41·2. 90 per cent. alcohol. 86 per cent. alcohol [a]o 147°2 [ab 164.4 R رة ج joogl

III. Properties of Maltodextrin.

Maltodextrin thus obtained appears to be a homogeneous product. It is a non-crystallisable syrup which can only be completely dried in a vacuum over phosphoric anhydride in the apparatus we described in 1897 (see Trans., 1897, 71, 76); in this condition, it is a colourless vitreous solid, somewhat hygroscopic, and soluble in hot water to an unlimited extent. It is soluble in alcohol of 85 per cent. to the extent of about 1 gram per 100 c.c., and is less sparingly soluble in alcohol of 90 per cent.

It possesses the following optical and reducing properties.*

The above specific rotatory power agrees very closely with the observations described in 1885 (loc. cit.), but the reducing power is considerably higher than the value, R 34.5, assigned to maltodextrin in the earlier work. We are unable to account for this discrepancy, and must be content for the present merely to record it.

Maltodextrin, notwithstanding its high reducing power, certainly does not contain any maltose as such, since, unless previously hydrolysed, it is not in the slightest degree fermentable with ordinary brewery yeast, and it does not yield a trace of crystallisable osazone with phenylhydrazine.

When a 5 or 10 per cent, aqueous solution of maltodextrin is digested for an hour at 50° with a few c.c. of malt-extract made from air-dried malt, hydrolysis proceeds very rapidly, and the products of the reaction (due correction, of course, being made for the malt-extract) approximate closely in properties to those of pure maltose.

It is only necessary to give the results of one such experiment, which is typical. A maltodextrin of $[a]_D$ 181·1° and R 42·8, on hydrolysis under the above-mentioned conditions, gave a solution with $[a]_D$ 141·0° and R 94·0, the properties of pure maltose for a similar concentration being $[a]_D$ 138·0° R 100·0. Phenylhydrazine now gave a large yield of highly crystalline osazone, which, when separated from the trace of glucosazone due to the sugars of the malt-extract, proved to be maltosazone with its usual melting point. The crystals agreed in form with the well-crystallised osazone given by pure maltose, and they were unmixed with the "isomaltosazone" forms which invariably occur when traces of dextrinous impurities are present (see

* It will be noticed that these values are not consistent with the "law of relation" which we have previously found to hold good between the optical and reducing properties of starch-products. We shall have more to say on this point, and on the "law of relation," on a future occasion:

Trans., 1895, 67, 731). These facts confirm us in our original opinion that maltodextrin is completely resolvable into maltose under the influence of diastase, and the want of complete accord of the optical and reducing properties of the hydrolysed maltodextrin with those of maltose is no doubt due to small errors of experiment incident to the hydrolytic process.

When maltodextrin is hydrolysed by treatment with an acid, it is completely converted into d-glucose, whose properties were identified by crystallising the sugar and determining its optical and reducing properties.

Evidence that the final product of hydrolysis of maltodextrin under these conditions consists exclusively of dextrose was obtained in various ways, as shown by what follows.

If maltodextrin is hydrolysed with oxalic acid, and the excess of acid is removed with calcium carbonate, the optical and reducing constants of the solution are consistent only on the assumption that nothing but dextrose is present.

Moreover, when such a solution of the hydrolysed products is fractionally fermented, it is found, on examining the solution at various intervals during the fermentation, that the optical and reducing properties of the substance which has disappeared, and of that which is left at any stage, conform to the known optical and reducing factors of dextrose.

In addition to this, we have carefully studied the quantitative relation of the dextrose formed to the amount of maltodextrin hydrolysed, in cases where the hydrolysis has been carried out with oxalic acid under the standard conditions fully described in the appendix to this communication.

The dextrose was in these cases determined by two independent methods, (1) by the increase in specific gravity during hydrolysis, and (2) by the cupric reduction of the product.

In this manner, it was found that 100 parts of maltodextrin, on complete acid hydrolysis, yield the following amounts of dextrose.

- 1.—By increase of sp. gr. 108.7 dextrose.
- 2.—By cupric reduction 106.0

IV. Oxidation of Maltodextrin.

The well marked reducing power of maltodextrin may be taken as evidence that its molecule contains the carbonyl group, and it therefore seemed probable that, by limited oxidation, it would yield a

hydroxy-acid or acids whose careful study might throw additional light on the constitution of the parent substance.

The method which gave promise of the best results was that of oxidation with yellow mercuric oxide in the presence of baryta; a process which, besides allowing of ready recovery of the products, admits of an estimation of the amount of oxygen used up in the reaction.

A known weight of the maltodextrin was dissolved in water, and to the solution, which was kept hot on a boiling water bath, freshly precipitated mercuric oxide was added, keeping it always in considerable excess; successive portions of a weighed amount of crystallised barium hydroxide were then slowly added so as to keep the solution just faintly alkaline. A portion of the liquid, filtered off from time to time, was tested with Fehling's solution, and the process was continued until no further reduction was apparent. It was always found that, as soon as the power of cupric reduction disappeared, the further addition of baryta to the hot neutral liquid caused a permanent alkalinity, and there was no further reduction of the mercuric oxide. The weight of the baryta added is a measure of the amount of oxygen used up in the oxidation, half an atom of barium corresponding to one atom of oxygen, or to the production of one carboxyl group in the mixed acids formed.

When maltose is oxidised under these conditions, we have always found that the end of the reaction with mercuric oxide corresponds almost exactly to the assumption of three atoms of oxygen by each molecule of the sugar.

On reference to a previous paper in which we have given careful determinations of the reducing power of maltose on Fehling's solution under standard conditions (Trans., 1897, '71, 100), it will be seen that the copper reduced also corresponds very exactly to the using up of three atoms of oxygen per molecule of maltose; hence there is a probability that the course of oxidation of maltose is the same no matter whether we use Fehling's solution or mercuric oxide and baryta.

The case, however, appears to be different when we come to maltodextrin. If, in this instance, we estimate the apparent amount of maltose in the maltodextrin, with Fehling's solution, that is, if we assume the maltose constituent of the maltodextrin has the same reducing power on Fehling's solution as free maltose, then the amount of oxygen consumed when maltodextrin is oxidised with mercuric oxide and baryta is always greater than the calculated amount, in the proportion of about 3 to 3.72. This difference may be due either to the oxidation of maltodextrin running a different course in the two processes, or to the fact that the maltose constituent of maltodextrin

is not oxidised in the same manner by Fehling's solution as is free maltose.

As an example of an experiment on the oxidation of maltodextrin with mercuric oxide and baryta, we may give the following.

84.28 grams of maltodextrin having a specific rotatory power of [a]_D 181.1 and a cupric-reducing power of R 42.8 were dissolved in 1000 c.c. of water, and the solution, after being heated in a porcelain evaporating dish on the water-bath, was treated with mercuric oxide and barium hydroxide in the manner already described. The point at which further reduction ceased was very sharply marked, and corresponded to the consumption of 62 grams of Ba(OH)₂+8H₂O, or 3.72 atoms of oxygen for every molecule of apparent maltose in the original maltodextrin, as determined from the value of R.

The decomposition of the barium salts and the complete separation of the barium, present certain special difficulties. Attempts to effect this by accurate precipitation with sulphuric acid are only partially successful, owing, in the first place, to a slight solubility of the barium sulphate in the dextrinous liquid, and, secondly, to the fact that a certain amount of the precipitate is in such an extremely finely divided state that it cannot be removed by ordinary filtration, and consequently it is impossible to accurately hit the point of complete decomposition of the salts.

After many trials, we have found the following method the best for surmounting these difficulties.

The solution of the oxidised products, after filtration, is cooled down, and a stream of carbon dioxide is passed through it in order to neutralise the very small excess of baryta present.* The solution of the barium salts of the organic acids is then evaporated to a thin syrup and the greater part of the barium is thrown out by adding dilute sulphuric acid.

The solution of acids containing BaSO₄ in suspension is then placed in a centrifugal machine, and the perfectly clear liquid, still, however, containing some barium, is poured off when complete separation has taken place, and is again evaporated to a fairly thick syrup. To this, about 1 c.c. of strong hydrochloric acid is added, and then a fair excess of sulphuric acid, the solution being kept cold. Under these conditions, the barium is completely thrown out of solution. A mixture of 95 per cent. alcohol containing some ethylic acetate is at once added. This precipitates the dextrin-like acids, which are then dissolved in a small quantity of water and again thrown out with alcohol and ethylic acetate. This process is repeated until all traces of mineral

[•] In some cases, the solution at this point was treated with hydrogen sulphide to remove any traces of mercury which might have passed into solution. As a matter of fact, however, no mercuric sulphide was ever obtained.

acids are removed, when the aqueous solution can be finally freed from the last traces of barium sulphate in the centrifugal machine.

The fractionation of the acids can then be proceeded with, but as they are much more soluble than the maltodextrin from which they are derived, fractionation with 95 per cent. alcohol is insufficient. Advantage can, however, be taken of their insolubility in ethylic acetate, and of the fact that they show a differential solubility in mixtures of ethylic alcohol and the acetate. The method we have usually employed is treatment of the crude acids with successive portions of hot alcohol by the process of digestion employed in the fractionation of the starch products, and then precipitation of the alcoholic solutions with ethylic acetate. By continuing this treatment through 20-30 fractionations, it was found possible to separate the dextrin-like acids derived from the oxidation of maltodextrin into two series, one, the more soluble portion, having a specific rotatory power of [a]_p 176°—179°, and the other with a rotatory power of [a] 189-192°. It is this second main fraction with the higher rotatory power, and constituting the larger amount of product, which we have submitted to detailed examination.

When in a pure state, it is an uncrystallisable, dextrin-like substance, having a specific rotatory power of $[a]_D$ 192·3°, and without the slightest reducing action on Fehling's solution. For convenience, we will provisionally refer to this acid as maltodextrinic acid A.

It has distinctly acid properties, and forms a well-defined, uncrystallisable calcium salt, which can be prepared by boiling a solution of the pure acid with calcium carbonate, and precipitating the salt with alcohol.

The calcium salt contains 2.4 per cent. Ca.

The great interest attached to this acid derivative of maltodextrin lies in the fact that it is hydrolysable both by diastase and by acids, giving, with the enzyme, a definite amount of maltose and an acid of lower molecular weight, whilst by acid hydrolysis it yields a definite amount of dextrose and a final acid of still less complexity.

V. Hydrolysis of Maltodextrinic Acid A with Diastase.

Under the ordinary conditions of hydrolysis with diastase, this acid yields maltose and an acid of lower molecular weight, which we shall refer to provisionally as maltodextrinic acid B.

The reaction was studied quantitatively in the following manner.

A solution of the A acid, containing about 5 grams per 100 c.c. was digested for 2 hours at 50° with 5 c.c. per 100 of a cold water malt extract made from air-dried malt. The specific rotatory power rapidly fell from $[a]_D$ 192.3° to $[a]_D$ 162°, at which it remained

constant,* the reducing power simultaneously rising from R. 0 to R. 40.0 (maltose=100). The solution gave a pure maltosazone on treatment with phenylhydrazine, and a further proof of the nature of the reducing substance was obtained by submitting the hydrolysed solution to fermentation with a little washed and pressed yeast. When the fermentation was complete, the optical activity and reducing power of the solution were redetermined, and from the differences between these and the original values two distinct estimations of the sugar fermented were made, on the assumption that it was maltose. The results were as follows.

			Grams of maltose
			fermented per 100 c.c.
Estimate	d fron	optical activity	2·290
,,	,,	reducing power	2-116

The concordance of these separate determinations leaves no doubt that the reducing substance produced by the diastasic hydrolysis of the A maltrodextrinic acid is maltose. The A acid has, therefore, yielded 40 per cent. of maltose and 60 per cent. of some other substance.

VI. Maltodextrinic Acid B.

This can be isolated from the products of the diastase hydrolysis of the A acid in the following manner.

The mixed products are fermented as completely as possible with a little washed yeast, and the residue, which is decidedly acid in character and amounts to 60 per cent. of the original A acid, is boiled with a little calcium carbonate. After filtration, the solution is evaporated, treated with dilute alcohol to remove a trace of proteids derived from the yeast, and the calcium salt is precipitated by more alcohol; this is further purified by re-dissolving it in water several times and throwing out by alcohol. At this point, the calcium salt was found to contain 3.1 per cent. of calcium, but as it was not yet quite pure, it was submitted to still further treatment. The salt is in the first place re-converted into the free acid by exact precipitation with oxalic acid. To the solution, filtered from calcium oxalate, tribasic lead acetate is added, and after separating a small precipitate which is formed, the solution is treated with hydrogen sulphide. The filtrate from the lead sulphide containing the acid is precipitated with strong alcohol, and the precipitated maltodextrinic acid B is repeatedly evaporated on the water-bath with alcohol until the acetic acid is completely removed. The acid is again con-

It is, of course, understood that the usual corrections were made for the malt tract.

verted into its calcium salt by boiling with calcium carbonate, and the salt is separated by alcohol precipitation.

It is a white, amorphous powder which, after drying at 100°, contains 3.8 per cent. of calcium.

VII. Acid Hydrolysis of Maltodextrinic Acids A and B.

Both A and B maltodextrinic acids yield definite amounts of dextrose on hydrolysis with acid, with the separation of a final residual acid which is identical in the two cases.

These reactions have been studied quantitatively by acting on a definite amount of the acids, or their salts, with oxalic acid, under the standard conditions described in the appendix. The amount of dextrose obtained from the free A acid in this manner was found in one case to be 85.8 per cent., and in a second 85.3 per cent. The calcium salt of the B acid, under similar conditions, gave 67.7 per cent. of dextrose.

The sugar, separated from the hydrolysed liquid by crystallisation, proved to be d-glucose, without the admixture of any other sugar.*

VIII. The Final Acid obtained by the Acid Hydrolysis of Maltodextrinic Acids A and B.

This acid is, with simultaneous production of dextrose, the final result of the acid hydrolysis of both the A and the B acids. We have obtained it from both sources, but it is of course more convenient to prepare it by direct acid hydrolysis of the A acid, without any intermediate use of diastase. It can be isolated from the products of oxalic acid hydrolysis by two methods. By the first, the solution, after neutralisation with calcium carbonate, is, in the first place, fermented to remove the dextrose, and is then evaporated and treated with strong alcohol to precipitate the calcium salt. By the second method, fermentation is avoided, the neutralised liquid, after evaporation, being treated with strong alcohol for the removal of the dextrose. On the whole, we prefer to omit fermentation.

The calcium salt thus obtained is further purified by precipitation from its aqueous solution with alcohol of 95 per cent. with the addition, as occasion demands, of a little ether. When alcohol alone is used, the salt is apt to come down very imperfectly and in such a very finely divided state that it remains suspended, forming a milky liquid.

^{*} In one of these experiments on the B calcium salt, the calcium oxalate which separated during hydrolysis was estimated. Its calcium was found to correspond to 3.8 per cent. of the salt taken, a result which agrees exactly with the direct determination of calcium in the original B salt.

This milk can, however, be made to "break" by shaking with a little ether. Where the object is purity of product rather than yield, the addition of the ether should be as far as possible limited.

The first preparation of the calcium salt of the final acid from the hydrolysis of maltodextrinic acid A gave $10\cdot1$ per cent. of calcium. By hydrolysis of the B acid, the salt was obtained also containing $10\cdot1$ per cent. of calcium. In the former case, the fermentation method had been employed.

By very careful and repeated fractionation of the calcium salt, a product was finally obtained containing 10.44 per cent. of calcium, but beyond this it was found impossible to go.

A combustion of this calcium salt with potassium dichromate in a stream of oxygen and air gave the following results.

0.2148 gave 0.2556 CO₂ and 0.1004 H₂O.
$$C = 32.4$$
; $H = 5.1$. $(C_5H_9O_6)_2Ca$ requires $C = 32.4$; $H = 4.9$; $Ca = 10.8$ per cent.

The study of this acid has been much facilitated by the discovery that the same final acid is present in considerable quantity amongst the products of oxidation of maltose by mercuric oxide and baryta. The oxidation of maltose was carried out in exactly the same manner as that of maltodextrin already described. The calcium salts of the acids obtained were hydrolysed with oxalic acid,* and the final acid was purified as a calcium salt in exactly the same manner as the final acid from the hydrolysed maltodextrinic acids.

In this state, two preparations gave, after drying at 100°, percentages of calcium equal to 10.4 and 10.5 respectively.

The latter preparation, on combustion with dichromate, gave the following results.

```
I. 0.2536 gave 0.3023 CO_2 and 0.1151 H_2O. C = 32.4; H = 5.0. II. 0.2131 ,, 0.2521 CO_2 ,, 0.0964 H_2O. C = 32.2; H = 5.0. (C_5H_2O_6)_2Ca requires C = 32.4; H = 4.9; Ca = 10.8 per cent.
```

There can be no question as to the identity of the final acids obtained by the oxidation and hydrolysis of maltodextrin and maltose respectively, as both their properties and their percentage composition are similar.

The acid itself, when liberated from its calcium salt, is a colourless syrup which shows no tendency to form a crystallised lactone. It is very soluble in water, but almost insoluble in alcohol of 95 per cent.

During this hydrolysis, considerable quantities of dextrose were liberated. The oxidation of maltose under the above conditions evidently results in the production of biose acids which are resolvable on hydrolysis into C₆- and C₅-groups. We are submitting this interesting fact to close examination.

Its cinchonic salt shows no tendency to crystallise, but the acid appears to form a crystallisable hydrazide, the only crystalline derivative we have been able, up to the present, to prepare. The calcium salt is very soluble in water, but quite uncrystallisable from that solvent; it has only a very slight influence on polarised light, and the actual amount of rotation is still doubtful.

The great obstacle to the extended examination of this acid has hitherto been the difficulty of its preparation in sufficient quantity; now, however, that its identity with the acid similarly obtained from maltose is put beyond all doubt, we shall be able to prepare it in considerable quantities and submit it to a careful study.

Taking into consideration the method of its formation, its source, and the empirical formula of its calcium salt, it would appear to be a normal carboxylic acid derived from a pentose. It has certain properties in common with xylonic acid produced by the oxidation of xylose, but our detailed study of the acid in question is at present too incomplete for us to speak positively on this point. It appears to us, however, that the preparation of a C_5 -derivative from a C_{12} -carbohydrate in the manner we have described is an interesting fact, and that in the limited oxidation and hydrolysis of polysaccharides of C_6 -sugars we may have an approach to an explanation of the formation of pentose derivatives by living plants.

In connection with this subject, we are also reminded of O'Sullivan's work on the arabinic acids (Trans., 1884, 45, 41; 1890, 57, 59; 1891, 59, 1029), in which he showed that arabic acid under the hydrolysing influence of dilute sulphuric acid yielded a series of acids of gradually diminishing molecular weight with simultaneous production of arabinose and in some cases galactose.

IX. Constitution of the Maltodextrinic Acids and Maltodextrin.

From its mode of preparation, and its behaviour under successive hydrolysis with diastase and oxalic acid, it is clear that maltodextrinic acid A, the main product when maltodextrin is oxidised with mercuric oxide and baryta, must be a carboxylic acid derived from a polysaccharide. Since the original polysaccharide, maltodextrin, is a reducing substance completely hydrolysable to maltose by diastase, it must be regarded as being made up of a certain number of C_{12} or maltose residues with the elimination of the elements of water, but still retaining, like maltose itself, a terminal COH group. If the process of oxidation of the polysaccharide consisted merely in the transformation of this terminal COH into carboxyl, we should expect to obtain an acid with its terminal C_{12} -group built up on the malto-

bionic acid type.* Such an acid, when treated with oxalic acid, would, like maltobionic acid, be transformed into glucose and gluconic acid, whilst under the action of diastase it would be almost certain to yield maltose and free maltobionic acid.

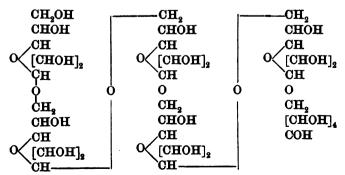
Although it is very probable that under the oxidising influence of bromins, maltodextrin may ultimately yield a complex acid of this constitution, it is evident that when mercuric oxide and baryta are used the oxidation proceeds much farther, and results in the splitting up of the terminal C_{12} -group into a C_{5} -acid residue which remains attached to the hydrolysable portion of the polysaccharide, and acids of low molecular weight which are separable by the subsequent treatment to which the complex acid is submitted during purification.

It has been shown by Scheibler and Mittelmeier (Ber., 1890, 23, 3060; ibid., 1893, 26, 2930) that the formation of reducing polysaccharides, that is, of compound saccharides with an aldose or ketonic structure of the terminal group, may be explained by the union, with elimination of the elements of water, of the carbonyl of one of the constituent groups with an alcohol group of another.

If we accept Fischer's constitutional formula for maltose as

$$CH_2(OH) \cdot CH(OH) \cdot CH \cdot [CHOH]_2 \cdot CH \cdot O \cdot CH_2 \cdot [CHOH]_4 \cdot COH$$

a polysaccharide corresponding to the empirical formula $\left\{ \begin{matrix} (C_{12}H_{20}O_{10})_2 \\ C_{12}H_{22}O_{11} \end{matrix} \right\}$, which we have hitherto employed for maltodextrin, will be represented by the union of three molecules of maltose, in the manner described above, with the elimination of 2 mols. of water. The constitutional formula of maltodextrin may then be represented as follows.



^{*} Maltobionic soid, $C_{12}H_{22}O_{12}$, was obtained by E. Fischer and Meyer by the oxidation of maltose with bromine (*Ber.*, 1889, 22, 1942). From the fact that it splits up, under the influence of dilute mineral acid, into d-glucose and d-gluconic

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This may be written in an abbreviated form thus,

$${\stackrel{O<{\stackrel{C_{12}H_{21}O_{10}}{C_{12}H_{20}O_9}}}{{\stackrel{C_{13}H_{21}O_{10}<...}}}}$$

The < is used, as suggested by Scheibler and Mittelmeier, to denote the open terminal COH-group. In this scheme, the C_{12} -groups are represented as linked to one another through oxygen atoms, and it is at these points that the elements of 2 mols. of water are introduced during diastase hydrolysis, with the formation of 3 mols. of maltose.

When the hydrolytic agent is an acid, the complex molecule behaves as though it were made up of C_6 -groups, also linked through the intermediary of an oxygen atom, and, just as in the former case, it is at these points that the elements of water are introduced, with the consequent production of glucose. Maltodextrin should therefore take up the elements of 5 mols. of water in order to be completely converted into glucose, 100 parts of maltodextrin yielding 109 of dextrose. How near this conclusion corresponds to the facts has already been shown (p. 293).

It may be objected that, according to the above constitution of maltodextrin, there seems to be no sufficient reason why diastase and acids should not both hydrolyse it to glucose, since, constitutionally considered, there is no apparent difference between the linkings of the C_6 -and C_{12} -groups.

There may, however, be a difference of spatial relations between the adjacent C_{12} -groups which may be sufficient to determine the differential action of the diastase, as contrasted with the absence of that action on the constituent C_{6} -groups, where we have every reason to believe the configuration is identical.

Another possible explanation may be found in the relative size or mass of the C_6 - and C_{12} -groups, which may have some effect on the result. We have probably an instance of this kind in the selective effect of the enzyme glucase on α -methyl-d-glucoside on the one hand, and α -methyl-xyloside on the other, as shown by Fischer (Zeit. physiol. Chem., 1898, 26, 68).

Of these two glucosides, one derived from a C₆- and the other from a C₅-sugar, and built up on an exactly similar plan, both constitu-

acid, the conclusion was drawn that maltobionic acid is derived from maltose by the oxidation of the terminal COH-group.

We have ourselves prepared maltobionic acid in the above manner, and have studied its products of hydrolysis quantitatively. These results which will be found described in the appendix to this paper, are fully confirmatory of the conclusions of Fischer and Meyer. tionally and stereochemically, the derivative of d-glucose is readily attacked by glucase, whilst that of xylose resists the action of the enzyme. The same difference also exists between the action of emulsin on the β -methyl-d-glucoside, and the β -methyl-xyloside respectively.

Possibly an investigation which we are making on the influence of the two enzymes, glucase and diastase, on maltodextrin may determine which of the above explanations is probable.

If the oxidation of maltodextrin resulted merely in the conversion of the COH-group into carboxyl, an acid would be formed the constitution of which, written in the abbreviated form, would be represented as follows.

$$0 < \begin{matrix} C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_{9} \\ C_{12}H_{21}O_{11} \end{matrix}$$

This would be the acid already referred to, which would almost certainly split up into maltose and maltobionic acid under the action of diastase, and into d-glucose and d-gluconic acid when hydrolysed with oxalic acid.

The constitution of maltodextrinic acid A certainly cannot be represented in this manner, for it yields a C_5 -acid on complete hydrolysis, not gluconic acid. The only explanation possible is that, during oxidation with mercuric oxide and baryta, the terminal C_{12} -group is attacked in such a manner as to remove, by simultaneous or successive oxidations, $C_7H_{12}O_5$, leaving the residue of a $C_5H_{10}O_6$ acid still in combination with the polysaccharide residue. The only possible constitution of the maltodextrinic acid A, and the only one which, as we shall presently see, is in consonance with all the known facts, is, the following,

$$O < C_{12}H_{21}O_{10} \\ C_{12}H_{20}O_{9} \\ C_{5}H_{9}O_{5}$$

The reducing C₁₂-group shown in the extended constitutional formula of maltodextrin has in fact now become

which is the residue of a normal carboxylic acid derived from a pentose.

When the maltodextrinic acid A is hydrolysed with diastase (I), and with oxalic acid (II), the reactions take the following course.

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In a similar manner, the B acid is also split up into glucose and the pentose acid under the action of oxalic acid, with the assumption of only 2 mols of water.

A careful examination of the facts which we have recorded in the experimental part of this paper will show that they are fully in accord with the above generalisations, as regards the composition, constitution, and reactions of the derivative acids. This is brought out more clearly in the following summary.

A Acid.—The calcium found in the purified salt was 2.4 per cent., which agrees exactly with the percentage of calcium in a salt of the composition $(C_{29}H_{49}O_{26})_2Ca$, the empirical formula for the salt of maltodextrinic acid A.

On hydrolysis with diastase, the A acid gave, in two experiments, 40.0 per cent. of maltose. The reaction I requires 42 per cent.

On complete hydrolysis with oxalic acid, the *A* acid yielded, in one experiment, 85.8 per cent. of glucose, and in another 85.3 per cent. The reaction II requires 88.4 per cent.

B Acid.—The calcium found in the pure salt was, in two separate preparations, 3.8 per cent. A salt of the composition $(C_{17}H_{29}O_{16})_2Ca$, the empirical formula of the B salt, should contain 3.9 per cent. of calcium.

The B calcium salt, on complete hydrolysis with oxalic acid, yielded 67.7 per cent. of glucose. Its theoretical yield is 70.7 per cent.

As to the empirical formula of the final C₅ acid, obtained by the complete hydrolysis of the maltodextrinic acids, there can be no doubt; but further investigation is necessary before we can positively state whether it is, as its mode of preparation would suggest, a normal carboxylic acid of a pentose.

The evidence as to the constitution of maltodextrin afforded by a study of its oxidation products seems to us conclusive, and it is further strengthened by the fact of the complete hydrolysis of maltodextrin to maltose under the influence of diastase, and by its yielding, within the experimental limits of error, the theoretical amount of glucose on treatment with oxalic acid.

This further study of the subject has served only to strengthen our previous views of the constitution of maltodextrin, although we must admit that some of the older evidence, such as that derived from the relation of optical activity to reducing power, and the molecular weight determinations, was not such as we should now deem conclusive.

We may still, if we choose, regard maltodextrin empirically as a combination of an amylon group with two amylin groups, and write its formula as $\begin{cases} (C_{12}H_{20}O_{10})_2\\ C_{12}H_{22}O_{11} \end{cases}, \text{ but we think that the new light we have now been able to throw on the subject justifies us in adopting another method of statement which is more in accord with our ordinary views of the structure of the more simply constituted carbohydrates. This formula in its abbreviated form is$

APPENDIX.

Acid Hydrolysis of Starch Derivatives.

An accurate determination of the amount of maltose or of glucose which a starch derivative will yield on complete hydrolysis with diastase and acid respectively is of great importance in determining the nature and constitution of the derivative. We have so frequently had occasion to describe minutely the method of procedure in the case of diastase-hydrolysis, and the processes for estimating the products, that it is quite unnecessary to enter again into details on this point. In the course of our more recent investigations, however, it became necessary to make frequent use of acid hydrolysis with estimation of the dextrose formed, and we had consequently to determine the best conditions under which such experiments could be carried out, and the magnitude of the experimental errors.

An estimation of dextrose when unmixed with any other optically active or reducing substance is now capable of being conducted with a high degree of accuracy. For the actual methods of estimation, we must refer to two of our recent papers in this Journal (Trans., 1897, 71, 72 and 275).

If we have a substance, such as a starch derivative, which is completely transformed into dextrose by the acid treatment, we have three different and independent methods of determining the dextrose formed:
(1) by observing the increase in the specific gravity of the solution after hydrolysis and making up to the original volume; (2) by the alteration in the optical properties of the liquid; and (3) by the increase in cupric-reducing power. Theoretically, these three methods should give identical results, practically it was found that there are certain small differences which had to be determined and corrected for.

One of the difficulties met with at the outset is that attendant on the

production of more or less of reversion products, which invariably tend towards a loss of reducing power, and to a smaller extent of optical activity. If these reversion products do not exceed about 5 per cent. in amount they have very little influence in altering the specific gravity, since their solution density is very nearly that of dextress.

Our first endeavour was to find a means of hydrolysis which would ensure complete conversion of the polysaccharides into dextrose with the minimum production of reversion products, and then to determine as far as possible the corrections necessary for these under certain standard conditions of hydrolysis as regards strength of acid, temperature of conversion, and time. After a considerable number of trials, with careful observations on the course of the reaction, we finally settled on the following standard conditions.

A solution of the carbohydrate under experiment, of a concentration of from 8 to 10 per cent., is hydrolysed with 2.5 grams per 100 c.c. of crystallised oxalic acid. The solution is contained in a pressure flask immersed in a boiling water bath, and the digestion is carried on at 100° for 14 hours.

In determining the sp. gr. of the hydrolysed solution, this must, of course, be corrected for the amount of oxalic acid present, but it is generally better to first remove this from the hydrolysed solution with calcium carbonate, evaporating somewhat, and making up to the original volume.*

When a definite amount of pure dextrose is treated in this manner, and the greatest precautions are taken to ensure accuracy in the cupric reduction experiments and in the weights and volume of the solutions, the dextrose determined by cupric reduction after digestion with the acid for 14 hours falls short of the amount taken by about 5 per cent. In one such experiment, where 9:309 grams of dextrose were taken, 8:923 grams were estimated in the hydrolysed liquid, a loss of 4:2 per cent. In another experiment, 8:550 grams of dextrose before acid treatment were estimated as 8:187 grams afterwards, a loss of 4:3 per cent.

This apparent loss is due to the formation of reversion products which have a lower cupric reduction than dextrose. Since we know that these products have a higher optical activity than dextrose, we should naturally be prepared to find a slight increase in specific rotation. This was, in fact, the case. The specific rotation of the dextrose in the first case increased from $[a]_D$ 52.6° to $[a]_D$ 53.2°, and in the second from $[a]_D$ 52.7 to $[a]_D$ 53.0.

^{*} In such experiments, the volumes are always deduced from the weighings and density.

On the other hand, there was no apparent change in the sp. gr. of the solutions before and after heating with the acid.

With these facts in view, it is possible to apply certain corrections to the results obtained when carbohydrates are hydrolysed under the standard conditions we have described. It must be understood that these corrections have been applied to the results which follow.

Hydrolysis of Maltose (anhydrous).

Dextrose produced from 100 parts of maltose.

1—By specific gravity	10 4 ·8.
2—By cupric reduction	103.71.
3—The theoretical yield of dextrose from	
100 parts of C ₁₂ H ₂₂ O ₁₁ is	105.26.

Hydrolysis of Soluble Starch, nC₆H₁₀O₅.

	I.	II.	III.	IV.
1-By specific gravity	109.4	110.9	110.2	
2-By optical activity	111.0	109.2		110.8
3—By cupric reduction	110.8	110.1		110.4

The soluble starch used in these experiments was submitted to a preliminary drying at 80°, and accurately weighed quantities of this were used for hydrolysis, the amount of water left in the preparation being determined by drying over phosphoric anhydride in the vacuum apparatus at 102—105°. The volumes of the solutions were deduced from the weights and specific gravity.

In experiments I and II, the determinations were made on the hydrolysed solutions still containing the oxalic acid. Expt. IV gives the results of a further examination of II, after removal of the oxalic acid with calcium carbonate.

The theoretical yield of dextrose from 100 parts of $nC_6H_{10}O_5$ is 111·1.

$$\textit{Hydrolysis of Maltodextrin,} \bigcup_{O < C_{12}H_{21}O_{10}}^{C_{12}H_{21}O_{10}} \underbrace{C_{12}H_{20}O_{9}}_{C_{12}H_{21}O_{10}}.$$

The results of this experiment have been already given in the body of the paper, but are here reproduced for purposes of comparison.

Dextrose yielded by 100 parts of maltodextrin.

1-By	optical activity	108.7
2-By	corrie reduction	106.0

The theoretical yield is 109 of dextrose.

Hydrolysis of Maltobionic Acid.

The test experiments on the hydrolysis of maltose and soluble starch show that the method gives results of a considerable degree of accuracy when certain corrections are applied which are constant under the standard conditions of experiment. It was felt desirable, however, to test the method also on an acid derivative of a polysaccharide which has some sort of relation to the maltodextrinic acids we have described. For this purpose, we prepared maltobionic acid by the exidation of maltose by bromine, as described by Fischer and Meyer (loc. cit.). Having prepared the lead salt, this was purified as far as possible by frequent precipitation from its aqueous solution by alcohol, then decomposed by hydrogen sulphide, and the free acid converted into the calcium salt. The calcium maltobionate was then purified still further by frequently precipitating with alcohol until its composition was constant.

Calcium in pure salt, 5.4 per cent., against 5.3 required by $(C_{19}H_{01}O_{10})_{0}Ca$.

On hydrolysing a definite weight of the dry calcium salt with oxalic acid, under the standard conditions, we obtained in one experiment a yield of 41.5 per cent. of glucose, and in a second experiment 42.6 per cent. The theoretical yield of glucose from $(C_{12}H_{21}O_{12})_2Ca$ on complete hydrolysis is 47.7 per cent.

DAVY-FARADAY RESEARCH LABORATORY, ROYAL INSTITUTION.

XXXI.—Attempts to Prepare Pure Starch Derivatives Through their Nitrates.

By Horace T. Brown, LL.D., F.R.S., and J. H. MILLAB.

The comparative ease with which certain nitrated derivatives of carbohydrates can be obtained, and the ready manner in which the NO_2 -groups can be subsequently removed by treatment with ammonium sulphide, induced us, some time ago, to turn our attention to a method which we hoped could be made applicable to the separation of the dextrins or maltodextrins which occur in restricted starch transformations by diastase. These substances differ so little in their relative solubility in alcohol of various strengths that the ordinary modes of separation are extremely tedious and difficult. The two important points to consider were the degree of ease with which the nitrates could be fractionated by treatment with various

solvents, and how far one could be sure that the recovered product obtained by the ammonium sulphide method represented the original substance before nitrification.

Although our hopes have only been partially realised, the work has not been without practical value, since by its aid, as will be seen in the following paper, we have obtained some indirect evidence as to the nature of the 'stable' dextrin of starch transformations. Apart from this comparatively small result, we believe that the work should be put on record as a guide to others who may be induced, like ourselves, to give a considerable amount of time to a subject which at the outset looks a promising one.

It is only by applying the method of nitration and recovery to starch derivatives of well-defined properties that we can hope to test its value. We have consequently applied it to (1) soluble starch, (2) the 'stable' dextrin after purification with alcohol, (3) amylodextrin, (4) maltodextrin, and (5) maltose.

Nitration and Recovery of Soluble Starch.

The soluble starch was carefully prepared from potato starch by Lintner's acid process. Twelve grams were nitrated at 0° with 70 c.c. of strong nitric acid, and the nitrate was precipitated in the first place with 70 c.c. of strong sulphuric acid, and afterwards with water. It was purified by dissolving it in ether and precipitating with chloroform. Analysis of the product by Lunge's method showed

1.—9.3 per cent. of nitrogen. 2.—9.1 per cent. of nitrogen.

The trinitrate of the empirical formula $C_{12}H_{17}O_7(NO_8)_8$ requires 9.1 per cent. of nitrogen.

Soluble starch was recovered from this nitrate by treating it at 70° — 80° , with water containing a little ammonium sulphide, and passing through the liquid a stream of hydrogen sulphide; under these conditions, the nitrate gradually dissolves with separation of sulphur, which, however, again goes into solution in an excess of hydrogen sulphide. The clear solution was then heated to the boiling point and the precipitated sulphur filtered off, using a hot funnel. When the concentrated filtrate was treated with an equal volume of 90 per cent. alcohol, a thick, slightly discoloured, flocculent precipitate was thrown down; this was re-dissolved in water and again precipitated with alcohol, the process being repeated several times until the product was obtained as a perfectly white, amorphous powder. The recovered starch had all the physical properties of ordinary soluble starch, giving the same pure deep blue colour with iodine. Its specific rotatory power was $\begin{bmatrix} a \end{bmatrix}_D 201.2^{\circ}$.

When a portion of this recovered starch was hydrolysed with malt extract at 55°, it behaved exactly as ordinary soluble starch does, the mixed products of transformation having a specific rotatory power of $[a]_D$ 151.8 and a cupric-reducing power of R 76.4.

The recovered product is, in fact, ordinary soluble starch in a state of great purity, and absolutely free from ash.

This process for the preparation of soluble starch can be recommended when a very pure specimen is required.

Nitration and Attempted Recovery of the Stable Dextrin.

The dextrin from which these preparations were made was obtained, as described in the next paper (Trans., 75, p. 317), by repeated alcoholic treatment of starch products hydrolysed to the lowest possible point by diastase. It is the stable dextrin of the so-called "No. 8 equation," frequently referred to in our previous papers. The properties of this dextrin will be fully described in a following communication. It was finally obtained with the following optical and reducing values: $[a]_{D}$ 195.0; R 5.5.

On treatment with nitric acid, exactly as described in the case of soluble starch, this dextrin yielded a nitrate in the form of a perfectly white powder, insoluble in water, but soluble in alcohol and ether or in a mixture of the two solvents. From such solutions, it is completely precipitable by chloroform. Fractionation of the product showed that it must be a mixture, since it was divisible into two portions containing 10·1 and 9·36 per cent. of nitrogen respectively.

Assuming the dextrin to have a composition corresponding to nC₆H₁₀O₅, its di-, tri-, and tetra-nitrates would require the following percentages of nitrogen.

Dinitrate	6·7	per o	nt. N	•
Trinitrate	9.1	,,	,,	
Tetranitrate	11.1		•	

It now remained to be seen if the original dextrin could be recovered from the mixed nitrates by applying the ammonium sulphide process, which had been so successful in the case of soluble

Owing to the recovered dextrin requiring stronger alcohol than soluble starch to throw it out of solution, it is much more difficult to completely free it from ammonia salts and fixed ash. These were finally removed by dialysis, and the recovered 'dextrin' was precipitated several times with alcohol until its optical properties were constant.

The optical and reducing values for the recovered product are here

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given for two distinct preparations, the values for the original dextrin being also given for comparison.

		[a] _D .	\mathbf{R} .
Original dextrin		195·0°	5.5
'Dextrin' recovered from ni	trates.		
Pr	ер. (1)	191.0	0
Pr	rep. (2)	188.4	0.4

Although at first sight it may appear that a non-reducing dextrin of high optical activity has been recovered, such is really not the If the reducing portion of the original dextrin with an R of 5.5 had been merely separated in the process of nitrification and fractionation, we should expect the specific rotatory power of the recovered 'dextrin' to be correspondingly increased, instead of being materially decreased, as it in fact is.

The distinct acid character of the recovered 'dextrin' is a proof that the original dextrin has been oxidised by the treatment with nitric acid, and that we have been really dealing with the nitrate of a polysaccharide acid, and not with that of the original dextrin, which is without acid characters.

This is a matter which will be found more fully dealt with in the next paper; it is sufficient for our present purpose to know that the nitration and recovery method is not applicable to the purification of the stable dextrin.

Nitration and Attempted Recovery of Amylodextrin.

The name amylodextrin was applied by W. Nägeli in 1874 to a substance which he obtained by the long-continued action of dilute mineral acids on ungelatinised starch in the cold. Unfortunately, of late years, a considerable amount of confusion has been introduced into the nomenclature of starch products by an application of the same name by C. J. Lintner and others to another substance which is identical with the 'soluble starch' of O'Sullivan, Musculus, and ourselves.

In 1889, one of us and Morris (Trans., 1889, 55, 449) described the results of an investigation of Nägeli's amylodextrin, and it was shown to be a well-defined substance belonging to the class of maltodextrins or amyloïns. It separates from its solutions in the form of sphæro-crystals, and has optical and reducing properties corresponding to $[a]_{\beta : 86}$ 206:1 and $\kappa_{3:86}$ 9:08 (= $[a]_D$ 192:0°, R 14:9)

It was regarded as constituted of six amylin groups combined with one amylon group, and consequently having the empirical formula $\left\{ \begin{array}{l} 6(C_{12}H_{20}O_{10}) \\ C_{12}H_{22}O_{11} \end{array} \right.$

In the light of our recent work on maltodextrin, described in the previous paper, the constitution of amylodextrin will doubtless be expressed in the abbreviated form by

$$\begin{array}{c} O < C_{12}H_{21}O_{10} \\ O < C_{12}H_{20}O_{9} \\ O < C_{12}H_{20}O_{9} \\ O < C_{12}H_{20}O_{9} \\ O < C_{12}H_{20}O_{9} \\ O < C_{12}H_{21}O_{10} < \end{array}$$

A part of the actual preparation of amylodextrin described in the 1889 paper was submitted to nitration under the usual conditions.

4.800 grams yielded 7.78 grams of nitrate (162 per cent.), which came down on successive treatment with sulphuric acid and water as a white, amorphous powder, very soluble in ether, acetone, and ethylic acetate, but insoluble in chloroform and light petroleum.

Three fractional precipitations were made with chloroform from its solution in ethylic acetate. These gave the following amounts of nitrogen.

Supposing it to be a true nitrated derivative of the unaltered amylodextrin, this corresponds very nearly with the 28-nitrate, which requires 11.0 per cent. of nitrogen.

The nitrate was treated in the usual manner with ammonium sulphide, and the recovered amylodextrin precipitated with alcohol; it was obtained perfectly free from ash, and in the form of minute sphærocrystals. The optical and reducing properties of the original and recovered products are here given.

	$[a]_{D}$	R.
Original amylodextrin	192.0	14.9
Amylodextrin recovered from nitrate	181.0	8.1

It is evident that the substance has been much altered during the process, and that the method of recovery is not applicable to amylodextrin.

Nitration and Attempted Recovery of Maltodextrin.

4.686 grams of carefully dried maltodextrin, on nitration, yielded 7.094 grams of the nitrate (151 per cent.). This is very soluble in 85 per cent. alcohol, and also in ether and ethylic acetate. From its

ethereal solution, it is thrown down by light petroleum in the form of oily drops, but is only partially separable by chloroform. Chloroform does not precipitate it from its solution in ethylic acetate, and light petroleum only partially.

The nitrate was fractionated by partial precipitation with light petroleum, evaporation of the mother liquors, re-solution in ethylic acetate, and further precipitation with light petroleum. Two fractions prepared in this manner gave the following amounts of nitrogen by Lunge's method.

The mixed nitrates, on treatment with ammonium sulphide, gave a substance which had the appearance of maltodextrin, but was of an acid nature and had been reduced in specific rotatory and reducing powers to

$$[a]_{D}$$
 185·1 R 26·3.

Alterations have, therefore, occurred during nitration, and the recovered product is not identical with the original.

Nitration and Attempted Recovery of Maltose.

The nitrate was readily obtained as a white, amorphous solid, which, after well washing with water, was re-dissolved several times in ethylic acetate and precipitated by chloroform, which brings it down as a syrup. This was separated, and after partial drying, the product was powdered and completely dried until the weight was constant. Lunge's method showed 13.9 per cent. of nitrogen in the purified substance. The hexanitrate, $C_{12}H_{16}O_5(NO_8)_6$, requires 13.72 per cent. nitrogen.

This nitrate did not yield pure maltose on treatment with ammonium sulphide, the specific rotatory power of the solution being very much higher than it should have been if the cupric reduction were taken as a measure of the maltose present.

Nevertheless, the presence of maltose in the mixture was ascertained by the formation of maltosazone.

General Remarks.

It will be observed that the regeneration of the original starch derivative in anything like a pure state from its nitrate was only found possible in one case, that of soluble starch. In all those

instances in which the starch derivative under experiment was cupric-reducing—that is, contained the open carbonyl group—the properties of the regenerated product indicated that more or less oxidation had taken place, and that the ethereal nitrate was an indeterminate mixture of a nitrate of the original carbohydrate and of a nitrated carboxylic acid or acids. This line of work, commenced in the early part of 1897, was consequently abandoned, since it did not promise to lead to the object we had in view, the separation and identification of the intermediate products of starch-hydrolysis.

Since that time an important paper on the nitration of carbohydrates has been published by Will and Lenze (Ber., 1898, 30, 68)
in which they give an account of their examination of most of the
principal carbohydrates from this point of view. They found that,
with the exception of the lactoses, most of them are readily converted
into nitrates, and in many cases these were obtained crystalline, and
with such well characterised properties, that the process may be used
for identification of uncertain carbohydrates and their recognition in
mixtures. An attempt to regenerate the original substance appears
to have been made only in one instance, that of Fischer's a-methylglucoside, whose tetranitrate yielded the parent substance when an
alcoholic solution was treated with ammonia and hydrogen sulphide.

Of the substances described in our present paper, the authors examined only starch and maltose. The former gave an amorphous hexanitrate, whilst from the nitrated products of the latter a crystalline substance was obtained whose nitrogen content corresponded to maltose octonitrate.

Had we been successful in obtaining definite nitrates of the intermediate starch derivatives, it was part of our plan to determine their molecular weight by the freezing point method. We have, in fact, made these determinations, but from what has been said it is evident that they are without value, and we consequently have not given them here.

We may, however, refer to the examination of the derivative of soluble starch from this point of view, since everything pointed to the derivative in this case being a perfectly definite trinitrate.

The determination was made in acetic acid, whose constant of molecular depression had been determined by means of naphthalene.

The result gave a value for M = 987. The molecular weight of $2[C_{12}H_{17}O_7(NO_8)_3]$ is 918.

From all we know about the constitution of soluble starch from other sources, it is quite certain that the value of n in the formula $n(C_{12}H_{20}O_{10})$ must be far greater than 2, so we must conclude that the freezing point method applied to such derivatives of the colloidal

carbohydrates as we are considering is quite inapplicable to the determination of molecular weight, and the same probably applies to the colloidal carbohydrates themselves.

THE DAVY-FARADAY RESEARCH LABORATORY,
ROYAL INSTITUTION.

XXXII.—The Stable Dextrin of Starch Transformations, and its Relation to the Maltodextrins and Soluble Starch.

By Horace T. Brown, LL.D., F.R.S., and J. H. MILLAR.

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I. Introduction.

It was shown by one of us and Heron in 1879 (Trans., 1879, 35, 596, that when gelatinised starch, or soluble starch, is hydrolysed with a little cold-water malt-extract at temperatures below 60° , the reaction proceeds with great rapidity until the mixed products of transformation show a cupric reduction corresponding to about 80 per cent. of maltose, and a specific rotation very close on $[a]_{\rm D}$ 150°.* With an active diastase, this point may be reached in less than 5 minutes, and further change is comparatively very slow indeed.

^{*} At ordinary temperatures, the specific rotatory power may be temporarily lower than this owing to the maltose being liberated in the birotatory state. (See Trans., 1895, 67, 309.)

This fact has been referred to many times in our papers, and was illustrated in the 1879 paper by a series of time curves, and again in the same manner in a paper on amylodextrin published in 1889 (Trans., 55, 457).

These values of $[a]_D$ 150 and R 80 mark, in fact, a definite resting point in the reaction, beyond which it is difficult to push it, unless a considerable amount of time is allowed.

That the cessation of action is due neither to the weakening of the enzyme nor to the action being a reversible one,* may be readily shown in a variety of ways. For instance, (1) the addition of more enzyme has no appreciable effect in hastening the very slow subsequent change after the resting point has been reached; (2) if more gelatinised starch or soluble starch is added to the solution, it is speedily brought to the same condition of optical activity and reducing power; (3) when a complete or partial separation of the maltose is effected by suitable means, as by fermentation or fractionation with alcohol, the residual dextrin shows the same resistance to further hydrolysis with diastase as—do the mixed products which have attained the resting stage.

In the 1879 paper (loc. cit.), it was also shown that, if we assume the whole of the reducing substance to be maltose, the resting point of the reaction corresponding to $[a]_D$ 150° and R 80 agrees very closely with the view that the starch has been hydrolysed according to the following empirical equation,

which requires 80.8 per cent. of maltose in the products of transformation.

This was the so-called 'No. 8 equation,' which at that time was supposed to represent only one of several other halting points in the hydrolysis. We are now of opinion that this well-marked resting stage, corresponding to $[a]_D$ 150, R 80, is the only one which admits, with certainty, of being expressed by any definite equation.

From the solution of the starch products which have been allowed to reach the above-mentioned point, crystallisable maltose can readily be prepared by extraction with alcohol of 80 per cent., or the maltose can be fermented out by yeast. By either of these methods of treatment, by far the greater part of the reducing substance may be removed, and in this respect these complete starch transformations stand in strong contrast with those in which the resting stage has not

^{*} By this we do not mean to imply a denial that the action may not be to some extent a reversible one, but only that this particular effect cannot be due to reversion.

been fully attained, since, in all incomplete conversions, the reducing constituent is not present wholly as crystallisable, fermentable maltose, but, in part, at any rate, as maltodextrins. Complete and incomplete conversions also differ from one another in their behaviour towards phenylhydrazine. If the transformation products have reached the resting stage corresponding to $[a]_D$ 150, R 80, the yield and purity of maltosazone is much greater than is obtained from a proportional amount of an incomplete transformation which might be assumed, from its reducing power only, to contain an equal amount of maltose. Indeed, all the available facts bear out the supposition that in a complete conversion which has attained the resting stage, the greater part, if not the whole, of the reducing power is due to free, crystallisable, and readily fermentable maltose.

Such a solution, besides maltose, contains an achroodextrin, which is precipitable by alcohol of 80—85 per cent. This dextrin, amounting to about 20 per cent. of the starch originally taken, is attacked only with difficulty by diastase, and differs in this respect from all the intermediate dextrinous products, amongst which is the maltodextrin which has been the subject of a previous paper.

We have submitted this stable dextrin to a careful re-examination during the past two years, and the present paper deals with our most recent conclusions with regard to its nature, properties, and constitution.

The difficulties of obtaining the stable dextrin in a state of purity are considerable, and even greater than they are in the case of maltodextrin. This arises from the fact that the process of treatment with alcohol necessarily tends to concentrate in the final insoluble product all impurities pre-existent in the starch and the transforming agent, which happen to be insoluble in the lowest strength of alcohol used in the separation.

If fermentation has also been employed, there is the additional risk of introducing small amounts of nitrogenous impurities, and also some of the non-volatile products of fermentation, although the latter are, for the most part, removable by the subsequent treatment with alcohol.

The actual amount of such impurities, which may amount to 2—3 per cent., can be determined with a close approximation to accuracy by submitting the separated dextrin to the standard methods of acid hydrolysis described in the previous paper (p. 305).

II. Separation and Purification of the Stable Dextrin.

In these experiments, we always commenced with from 2000 to 3000 grams of well-washed potato starch, which was brought into VOL. LXXV.

solution with from 16 to 20 litres of water by successive gelatinisations and liquefactions, in the manner described in our previous paper on maltodextrin (this vol., p. 288). We thus obtained the starch solids, for the final conversion, at a concentration of from 12 to 15 per cent. The preliminary conversions at 65-70° were allowed to go sufficiently far to prevent any of the higher starch transformation products coming out of solution when the temperature was reduced to 15-20°. The completion of the conversion down to the 'resting point,' corresponding to [a] 150°, R 80, was then carried out at the ordinary temperature, with the aid of coldwater malt-extract, made from a very diastasic air-dried malt. conversion sometimes lasted for two days * or more, the object being to select the best conditions for producing a low conversion, with the employment of the minimum amount of malt-extract. The importance of this condition is rendered evident by what we have already said about the concentration of impurities on the dextrin during the subsequent processes of its extraction.

The actual amount of 'normal' † malt extract required was from 3 to 6 c.c. of the extract per 100 c.c. of a solution containing from 9 to 15 grams of starch products. This is equal to from 0.3 to 0.4 c.c. of extract per gram of starch converted, and represents about the minimum amount which can be used for these complete conversions. The actual amount of solids introduced with the malt-extract represents about 3.5 per cent. of the starch used, but by far the greater part of these solids are separable by alcohol of from 75—90 per cent., and are removed in the processes of purification to which the dextrin is submitted.

After the conversion had been run down to the desired point, the solution, filtered from a certain amount of 'starch-cellulose,' which always separates during starch transformations made in the cold, was evaporated to a thick syrup. The process of separation was then commenced; this consisted of fractionation with alcohol of various degrees of strength with occasional recourse to fermentation. The treatment with alcohol was varied in every conceivable manner.

It would be tedious and unprofitable to give anything but a mere sketch of the process, since, at this stage, it did not differ materially from similar methods we have frequently described before, except as regards the number of operations and the length of time required, often amounting to several months for each experiment.

^{*} The solution was occasionally sterilised, with the further addition of malt extract.

^{† &#}x27;Normal' malt extract is obtained by digesting finely divided malt (air dried) with 2.5 times its weight of cold water, and filtering after 6 hours.

We will briefly describe the course of one experiment, which is typical of all.

A conversion of 2400 grams of starch which had been run down to the 'resting stage' and evaporated to a syrup was treated in the first place with 7 litres of hot alcohol of 90 per cent.,* the strength of the alcohol in the mixture being 75—80 per cent.

About 200 grams of dextrin separated. The alcoholic solution, poured off when cold, was distilled, and the syrupy residue poured into 6 litres of boiling spirit of 95.5 per cent., and digested for some time. The second dextrinous residue thus obtained was further digested with 85 per cent. spirit, the insoluble portion being added to the original residue of 200 grams. The alcoholic solutions on distillation yielded a syrup from which maltose readily crystallised.

The combined dextrinous portions, amounting to 660 grams, now contained only 42 per cent. of maltose, as against 80 per cent. in the original starch transformation products. This crude dextrin was dissolved in 6 litres of water, and the solution, having a sp. gr. of 1042.6, was set to ferment with 15 grams of washed and pressed yeast. During the progress of the fermentation, which lasted for 10 days, an examination of the solution was made from time to time, and it was shown that, whilst the specific rotatory power of the unfermented matter steadily increased, the optical properties of the portions fermented at any stage corresponded with those of maltose.

The fermented solution, which now gave only a trace of insoluble osazone on treatment with phenylhydrazine, was evaporated to remove alcohol. The specific rotatory power of the residue was $\begin{bmatrix} a \end{bmatrix}_0 182.5^\circ$.

In order to remove any trace of maltodextrin, the solution, made up to sp. gr. 1043, was now once more treated for 2 hours at 50° with 40 c.c. of a very active malt extract. It was then once more heated to the boiling point, cooled, and again set to ferment with 11 grams of washed yeast for 5 days, during which time 14.04 grams of fermentable substance disappeared, which represents about 3.0 per cent. of the 540 grams of the crude dextrin. The optical properties of this fermentable substance were again found, by the usual process of fractional fermentation, to correspond with those of maltose.

Two precipitations were then made with 85 per cent. alcohol, and the dextrin obtained was submitted to nine successive extractions with boiling alcohol, each extraction lasting for a day or more, the mixture being frequently agitated. The first six of these extractions were made with alcohol of 85 per cent., and the other two with alcohol of 80 per cent. The weights and specific rotatory powers of the matter extracted, and the specific rotatory power of the residual dextrin after each extraction, were determined.

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^{*} Throughout the paper, the percentages of alcohol are expressed by volume.

The results of the nine successive treatments at this stage are here tabulated.

The amount of crude dextrin at the commencement was 492 grams.

	1481	4E 1.		
N. 6.6	Extracted with alcohol.		Residual dextrin.	
No. of fraction.	Weight.	[a] ^D .	[a] ^D .	
80 per 85 per cent. cent. spirit. spirit. 6 & 2 9 9 7 8 8 7 1	Grams. 10 '66 8 '14 9 '39 9 '63 2 '51 7 '07 22 '12 22 '34 17 '11	115·7° * 127·3 * 145·7 166·3 167·1 168·2 174·6 166·9 177·7	185·3° 186·9 186·8 186·7 188·2 187·5	

TABLE I.

It was evident that the method of separation adopted up to this point had practically reached the experimental limits, so a different plan of treatment was now adopted.

The dextrinous residue, after the ninth treatment, amounting to 383 grams of substance with an $[a]_D$ of 186.8° , was dissolved in 1000 c.c. of water, and cold alcohol of 85.5 per cent. was gradually added, until precipitation just commenced. The precipitate containing albuminous matter was rejected. Alcohol of 85.5 per cent. was again added with constant agitation, until about one-third of the dextrin was thrown down. This is fraction A, and it was separately treated by dissolving it in its own weight of water, and precipitating in two fractions, A_1 and A_2 , by the further addition of 85 per cent. spirit.

These fractions had the following properties.

$$A_1$$
 [a]_D 193·1 R 5·6 A_2 [a]_D 193·0 —

The clear solution from A was again precipitated in the cold with alcohol. On heating, the precipitate redissolved, but was again thrown out on cooling—this is fraction B. After the removal of the precipitate, the liquid was increased in alcoholic strength, in the first place to 85 per cent., and in the second to 95 per cent., the fractions thus obtained being C and D. The final mother liquor from D was mixed with that from A_2 , and the 55 grams constituting fraction E were

^{*} These extractions contained the non-volatile products of fermentation and the sugars of the malt-extract.

freed from alcohol and separated into two parts, E_1 and E_2 , with 95 per cent. alcohol. These latter fractions had the following specific rotatory power.

Fraction B

$$[a]_D$$
 192·1°
 Fraction E
 $[a]_D$ 184·9°

 C
 $[a]_D$ 190·8
 E
 $[a]_D$ 186·5

 D
 $[a]_D$ 189·0
 E
 $[a]_D$ 179·7

It is clear from the above that the dextrin which could not be further separated by the nine treatments with alcohol described in Table I has given way to the modifications in the alcohol treatment just described, products being obtained amongst the least soluble portions with specific rotatory powers as high as $[a]_D$ 193.0°.

The above fractions A_1 , A_2 , B, C, and D, with rotatory powers of from $[a]_D$ 189.0 to $[a]_D$ 193.1 were now united and subjected to still further treatment.

After being evaporated to a thick syrup, they were gradually treated with 2 litres of hot 86 per cent. alcohol; after digestion for 6 hours, the alcoholic solution, when cold, was poured off, and the properties of the residue, and those of the small quantity of extracted matter, were examined. These were as follows.

Dextrinous residue.......
$$[a]_D$$
 192·7°
Portion soluble in alcohol... $[a]_D$ 183·6

This process was repeated twice more, and the dextrin, which had now been reduced to about 200 grams, was obtained with a specific rotatory power of $[a]_D$ 192.0°.

We now once more resorted to fractionation. The 200 grams of dextrin were dissolved in 500 c.c. of water, and 500 c.c. of alcohol added in the cold; the addition of 100 c.c. more of 96 per cent. alcohol brought down fraction \mathbf{F} ; this, when redissolved in 200 c.c. of water and again treated with 250 c.c. of 96 per cent. alcohol, gave a precipitate which, by further similar treatment, was resolved into fractions \mathbf{F}_1 , \mathbf{F}_3 , and \mathbf{F}_4 , having the following optical and reducing properties.

It must be remembered that, in the protracted and laborious treatment of separation, which is here only described in a very condensed form, every conceivable variation of treatment with alcohol was adopted, whilst the process was further supplemented by occasional treatment with diastase to break down any maltodextrin which might remain adherent to the product, and also by employing fermentation to assist in the elimination of the maltose.

In all similar experiments, no matter how long the alcoholic fractionation may have been continued, we have always obtained the same final result. A point is ultimately reached, sometimes comparatively speedily, when no further change takes place in the properties of the separated dextrin. This is marked by the product assuming optical and reducing properties corresponding to

Such a product is, however, never quite free from ash, which amounts to 0.3 to 0.5 per cent. of the dry weight, and it also contains a trace of nitrogen corresponding to about 0.2 per cent. of albuminoids. Hence the above values of $[a]_D$ and R are slightly lower than those corresponding to the pure carbohydrate; the error introduced from this cause does not, however, exceed more than 2° in the specific rotatory power, and will have no appreciable effect on the value of R.

Prepared in this manner, this dextrin is obtained as a white, amorphous, gummy substance, soluble in water to any extent, and completely separable from its aqueous solutions in the cold by alcohol of 80 per cent., which brings it down as a waxy solid with a silky lustre.

Dried at 100° in a vacuum over phosphoric anhydride, it has a divisor of 3.995 for a solution density of 1054.49.

One of the chief characteristics of this dextrin, prepared from starch conversions which have attained the 'resting stage,' is the relative difficulty with which it is attacked by diastase, as compared with the small power of resistance exhibited by the intermediate products. The mode in which it breaks down under the agency of dilute acids, and the long continued action of diastase, will be described later on.

III. Is the Stable Dextrin a Reducing Substance?

We have already stated that the final product obtained by protracted treatment with alcohol, assisted by fermentation, always possesses a reducing power of about R 5.5, and we have now to consider whether this is inherent to the dextrin itself, or whether it may not, after all, be due to an admixture of from 10 to 15 per cent. of compounds of the maltodextrin class which have persistently adhered to it through all the long processes of treatment to which it has been subjected. The reducing power certainly cannot be due to maltose itself, since the purified dextrin gives no trace of maltosazone when treated with phenylhydrazine, neither does it contain any substance directly fermentable with yeast.

If the stable dextrin in a state of purity is a non-reducing substance,

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it is possible to deduce its optical properties from an analysis of the mixed products of a starch transformation which has been carried down to the 'resting stage.' With the improved methods of analysis which we have described in a previous paper (Trans., 1897, 71, 72), it is possible to determine this value with considerable accuracy, for under these conditions complete corrections can be made for the transforming agent (malt-extract) employed, and for the small amount of ash existing in the original starch. After fractionation, these corrections cannot, of course, be applied with the same degree of accuracy.

We have made two such experiments for the determination of the specific rotatory power of the stable dextrin, on the assumption that it is non-reducing.

It is necessary, in the first place, to determine very exactly the total weight of the starch products per 100 c.c. of the liquid after complete transformation. This is effected by correcting the specific gravity for that due to the malt-extract, and then employing the particular 'divisor' corresponding to the phase of transformation and the concentration of the solution.

The 'divisor curve' for a transformation corresponding to [a]_D 150, R 80 has been accurately determined for concentrations of from 2.4 to 22.3 per cent. of solids, and will be found at p. 80 of our previous paper on "Experimental Methods" (Trans., 1897, 71, 72). In such experiments as we are describing, where the highest degree of accuracy is necessary, a further small correction was necessary for the 0.2 per cent. of ash which the original starch contained.*

The amount of apparent maltose per 100 c.c. was then determined from the cupric reduction, due correction being, of course, made in all cases for the reduction due to malt-extract.

The amount of rotation corresponding to the maltose was then calculated from the known optical constants of the maltose at the particular concentration, and the value thus obtained was deducted from the total (corrected) optical activity of the original solution. The remainder represented the rotation due to the dextrin, the amount of which was also known by subtracting the known amount of maltose from the total (corrected) starch solids per 100 c.c.

We thus have all the elements necessary for the calculation of the specific rotatory power of the dextrin.

To ensure the greatest possible accuracy, the volumes of the liquid were deduced from weighings and densities, and the cupric reductions, several times repeated, were also made on weighed amounts of the solutions.

^{*} This correction only affects the divisor in the third decimal place. For instance, the divisor from the curve being 3.958 for sp. gr. 1038-61, becomes, when corrected for 0.2 per cent. of ash, 3.954.

In the first experiment, the mixed transformation products corressponded to $[a]_D$ 150·3, R 79·6, and in the second to $[a]_D$ 150·4, R 79·0.

The estimated specific rotatory power of the stable dextrin, assuming it to be non-reducing, came out as follows.

(1)
$$\begin{bmatrix} a \\ b \end{bmatrix}_{D} 201.8^{\circ} \\ (2) \begin{bmatrix} a \\ b \end{bmatrix}_{D} 200.0 \end{bmatrix}$$
 Mean. 200.9° .

The properties of the dextrin which we obtained by continuous fractional treatment of the starch transformation products corresponded, as we have seen, to R 5.5 to 5.9 and $[a]_D$ 195° to 196°, with a possible error of $+2^\circ$. These properties are quite consistent with a mixture of 94.5 per cent. of a non-reducing dextrin with an $[a]_D$ 200.9°, and 5.5 per cent. of maltose or its equivalent of maltodextrin. Theoptical properties of such a mixture would correspond to $[a]_D$ 197.4°. We are, however, by no means justified in concluding that the dextrin obtained really consists of such a mixture, and must seek further evidence in other directions.

In the paper of 1885 on the "Non-Crystallisable Products of Starch Transformation," by one of us and Morris (loc. cit.), a process was described by which the residual reducing power of dextrins, previously separated by alcoholic fractionation, could be completely destroyed, and the apparently unaltered dextrin recovered in a non-reducing state. This method consisted in acting on the dextrin with Knapp's mercuric cyanide solution, and subsequently acidifying with hydrochloric acid and separating the mercury with hydrogen sulphide, the dextrin being afterwards separated from the filtrate by precipitation with alcohol. Since the optical properties of the dextrins were somewhat increased by this process, and their behaviour under hydrolysis with diastase was apparently unaltered, it was believed that a separation had been effected between the dextrin and the substance to which it originally owed its reducing power.

In 1890, Scheibler and Mittelmeier, in a valuable and highly suggestive paper on starch products (Ber., 1890, 23, 3060), objected to this method on the ground that, if the dextrin were in itself a reducing substance, its aldehydic group would necessarily be oxidised, and that the resulting product would be an acid, and not the original unaltered dextrin. Unfortunately, the value of the experimental portion of the paper is much lessened by the fact that Scheibler and Mittelmeier made use of a commercial dextrin, which from their description must have been a torrefaction product of starch, at all times a very indeterminate substance, whose nature and relation to the dextrins of starch transformations has never been worked out.

Nevertheless, the criticism of the method we employed to destroy the reducing power is perfectly just and well founded, as will be seen by a perusal of our recent paper on maltodextrin (this vol., p. 286), which contains the first experimental proof that a reducing starch product can give rise, on oxidation, to well-defined polysaccharide acids. It was the fact that these complex acids have such feeble acid properties, and resemble the parent substance so closely in optical properties and in their behaviour towards diastase, which caused us to overlook their formation in our work of ten years ago.

In the light of this work on maltodextrin, it appeared to us that the question whether the reducing power of R 5.5 possessed by the stable dextrin after repeated treatment is really inherent to the dextrin molecule, and is not due to admixture with something else, ought to be settled by oxidising the dextrin with mercuric oxide and baryta to the point of disappearance of its reducing power, and then once more fractionating the product. If the reducing power is due to a foreign substance, it is this alone which will be oxidised, and the acid or acids so formed ought to be separable from the dextrin which will be left as a neutral substance. If, on the other hand, the reducing power is inherent to the dextrin molecule, we ought to obtain a complex 'dextrinic acid' which will not give way to fractionation.

We have carried out this experiment several times with results which, we think, leave no doubt as to which supposition is correct.

IV. Oxidation of the Stable Dextrin and Formation of Dextrinic Acid.

A preparation of the stable dextrin with [a]p 195.0, R 5.5 was oxidised with mercuric oxide and barium hydroxide under the conditions employed for the oxidation of maltodextrin (this vol., p. 293). It was found that 70 grams of the dextrin with an excess of mercuric oxide required the gradual addition of 4.27 grams of crystallised barium hydroxide, Ba(OH), +8H,O, to completely destroy its power of reducing Fehling's solution.

After filtration, the solution, slightly acidified with sulphuric acid, was again filtered, and the product was recovered by several precipitations with alcohol of 80 per cent. At this point, the oxidised dextrin had a specific rotatory power of [a] p 192.5°.

It was then partially precipitated three times successively with alcohol of 75, 84, and 85 per cent. The properties of the several fractions were

	[a] _{D.}	R.
1.	$193 \cdot 2$	0
2	192 ·0	0
3.	192.0	0

Although quite free from sulphuric acid, the solutions were distinctly acid to test paper.

It was now attempted to split this oxidised dextrin further by dissolving it in 50 per cent. alcohol and fractionally precipitating with a 5 per cent. solution of barium hydroxide in 50 per cent. methylic alcohol; the precipitated barium compounds were then separately treated, first with carbonic anhydride, and afterwards with dilute sulphuric acid in the cold, the oxidised dextrin being recovered from the filtrate by precipitation with alcohol.

The products thus obtained had specific rotatory powers varying only between $[a]_D$ 193·2° and $[a]_D$ 193·6° R 0. They were quite dextrinous in their physical characters, but all had a very distinct acid reaction, from which the parent dextrin was quite free.

The oxidised dextrin, which we shall in future refer to as dextrinic acid, when dried in a vacuum over phosphoric anhydride, gave a divisor of 4.000 for a solution density of 1039.0. It was not quite free from ash, so at this stage it was not found practicable to determine its molecular weight from its barium or calcium salt.

On hydrolysis with oxalic acid,* 100 parts of dextrinic acid yielded 105.9 parts of glucose, as against 108.8 parts yielded by the original dextrin (vide infra).

V. Nitration and Subsequent Recovery of Dextrinic Acid.

We have shown in a previous paper (this vol., p. 310) that when the stable dextrin is nitrated, the nitrate, on treatment with ammonium sulphide, yields a non-reducing substance with acid properties, not the original dextrin from which we started. We have found, however, that the dextrinic acid which is obtained by the oxidation of the dextrin with mercuric oxide and baryta is itself capable of nitration, and that the dextrinic acid can be readily regenerated from the nitrate in the usual manner, and with all its properties unchanged.

By this process, we are able to obtain the dextrinic acid quite free from ash, and consequently in a state suitable for the examination of its salts.

^{*} The standard time of hydrolysis of 14 hours was not found sufficient to completely hydrolyse the dextrinic acid, which required 24 hours treatment under the conditions described in the Appendix to our paper on maltodextrin (this vol., p. 305).

A specimen of dextrinic acid with an optical activity of [a] 193°, and yielding 105.9 per cent. of glucose on complete hydrolysis with oxalic acid, was obtained as a thick syrup on concentrating its solution to the utmost on the water-bath. It was then mixed in the cold with ten times its weight of strong nitric acid, sp. gr. 1.4, and the nitrate thus formed was precipitated by strong sulphuric acid and subsequent dilution with water in the usual manner, the temperature being maintained as low as possible by immersing the vessel in ice The nitrate, after being well washed with water, was dissolved in glacial acetic acid and filtered; water added to this solution again threw out the nitrate, which was once more dissolved in acetic acid and reprecipitated. This operation was twice repeated, and the nitrate was then treated with ammonium sulphide; the recovered dextrinic acid was completely freed from ammonium salts by repeated precipitations with alcohol of 95 per cent., seven or eight such treatments generally being necessary before the Nessler test ceased to give a reaction. It was finally obtained in a state of purity, and quite free from ash, as a white, amorphous substance having feeble but distinct acid properties, and with a specific rotatory power corresponding to [a]_D 193.7° and R 0 against [a]_D 193.0° of the original acid before nitration. After completely drying in a vacuum at 100° over phosphoric anhydride, its divisor for a solution density of 1040:36 was found to be 4:005.

On complete hydrolysis with oxalic acid, it yielded 106.2 per cent. of glucose, against 105.9 given by the original dextrinic acid before nitration.

This experiment is an important one, not only in showing that the product recovered from the nitrated dextrinic acid is identical with the dextrinic acid before nitration, but also in showing that the acid properties of the oxidised dextrin cannot be due to the accidental admixture of other acids produced by the oxidation of a reducing carbohydrate present in the original dextrin. Were this the case, we should have to assume that the acids proceeding from this reducing carbohydrate not only persistently adhere to the dextrin during the repeated fractionations of dextrinic acid itself, but that even the process of nitration, fractionation of the nitrate, and the subsequent processes of recovery have also been incapable of effecting differentiation.

In the face of all this evidence, we think it can no longer be doubted that the carboxylic constituent of the oxidised dextrin really forms part of the molecular complex constituting dextrinic acid. To admit this fact is, of course, to admit that the aldehydic or ketonic portion of the original dextrin, to which it owes its reducing power of R 5.5, is also part of the molecular complex of the stable dextrin.

VI. Analysis of the Calcium Salt of Dextrinic Acid.

We have already stated that dextrinic acid possesses only very feeble, although well-marked, acid properties. It readily forms barium and calcium salts on boiling the acid with the respective carbonates, and these salts can be precipitated from the solution by dilute alcohol. They are readily soluble in water, but like the corresponding derivatives of the maltodextrinic acids, they cannot be obtained in the crystallised form.

Owing to its complexity and feeble basicity, the dextrinic acid must be absolutely free from ash before it can be used for the preparation of its salts, otherwise their composition could not be even approximately determined.

The process of nitration of the acid and its subsequent regeneration from the nitrate fortunately enables us to prepare the dextrinic acid in this state and in a high degree of purity.

An analysis of the calcium salt after most careful preparation in this manner shows that it contains 0.29 per cent. of calcium.

VII. Hydrolysis of Dextrinic Acid with Oxalic Acid and Diastase.

We have already seen that when free dextrinic acid is completely hydrolysed with oxalic acid, the main product is glucose, which amounted in one experiment to 105.9 per cent. and in another to 106.2 per cent. The hydrolysis of the calcium salt in a similar manner was found to produce 107.2 per cent. of glucose on the dry salt.

It was always found in such experiments that, besides glucose, the complete hydrolysis gave rise to a small quantity of an acid of low molecular weight, the production of this final acid being strictly analogous to that of the C₅-acid when the maltodextrinic acids are hydrolysed, or to that of gluconic acid when maltobionic acid or its salts are treated with dilute acids.

The large yield of glucose in the case of the dextrinic acid hydrolysis clearly shows that the carboxyl portion of the original complex must bear a very small relation to the total molecule, a result which is also quite in accord with the small reducing power of the dextrin from which the dextrinic acid has been derived.

Since we could not expect more than a 2.5 per cent. yield of the final acid, it was necessary to hydrolyse a considerable quantity of the dextrinic acid in order to obtain a sufficient quantity of this substance to admit of a study of its properties.

In order to see if it were gluconic acid, the mixed products from the hydrolysis were fermented with yeast, and the residue, after

evaporation and treatment with calcium carbonate, was evaporated with alcohol and fractionated in such a manner as to separate any trace of calcium gluconate. No evidence of its existence could be obtained, although it had been shown in preliminary experiments that even an extremely small quantity of previously added calcium gluconate could be recovered in a crystalline form by the method adopted.

A sufficient quantity of the final acid for complete examination was prepared by completely hydrolysing 29 grams of dextrinic acid by heating it with a 2.5 per cent. solution of oxalic acid for 23 hours at 100°. The solution of the hydrolysed products, after treatment with calcium carbonate, was filtered and evaporated to the thickest possible syrup, which was then repeatedly extracted with hot 95 per cent. alcohol to remove the glucose.*

The residual calcium salt was redissolved in a small quantity of water, filtered, and again thrown down with alcohol; at this stage, the salt which was evidently still impure, contained 9.0 per cent. of calcium. After several further treatments of a similar kind, and a partial fractionation with alcohol, the salt was obtained with constant properties. The following results were obtained on analysis.

	Carbon.	Hydrogen.	Oxygen.	Calcium.
Calculated for $(C_5H_9O_6)_2Ca$	$32 \cdot 4$	4.9	51.8	10.8
Found		5.3	52·0	10.56

The salt corresponds in composition and general properties with the final C₅-acid which we obtained by complete acid hydrolysis of the two maltodextrinic acids, and also with the acid obtained by the oxidation of maltose with mercuric oxide and subsequent hydrolysis of the product (this vol., p. 296).

Dextrinic acid and its salts, unlike maltodextrinic acid A, are but very slowly influenced by diastase. A marked action can, however, be detected if the digestion with malt extract in the cold is allowed to go on for several days, or if the amount of diastase used is relatively large, and the action is carried on for 48 hours or so at 50—60°.

The product of hydrolysis in this case is a mixture of maltose and glucose, a fact which will be further considered in the next section in connection with the diastase-hydrolysis of the parent dextrin itself.

* The glucose was crystallised out from these alcoholic extracts. It proved to be d-glucose.

VIII. Hydrolysis of the Stable Dextrin with Oxalic Acid and with Diastase.

When the stable dextrin is hydrolysed with a 2 per cent. solution of oxalic acid under the standard conditions, it is completely converted into d-glucose. We here give the result of such an experiment, the glucose being determined by two independent methods.

Glucose from 100 parts of dextrin.

1.—Estimated	by increase of sp. gr	110.8
2.— "	from cupric reduction	108.9

The well-marked 'resting stage' of the products of starch transformations brought about by diastase, when these products have reached an [a]_D of 150° and R 80, has already prepared us for the fact that the dextrin, when isolated, has a considerable resistance to the hydrolytic influence of diastase. The observed difference in the rapidity of this action on the dextrin, on the one hand, and on maltodextrin or any of the intermediate transformation products, on the other, is very striking. Whereas solutions of maltodextrin of a concentration of from 5 to 10 per cent. are completely resolvable into maltose by about half an hour's digestion at 50° with an amount of malt extract corresponding to but 2 or 3 c.c. per 100 c.c. of solution, a dextrin solution requires several hours of similar treatment with ten times the amount of hydrolysing agent before even an appreciable amount of change is produced.

We have made this experiment several times, with every necessary correction, and have found that a solution of the stable dextrin of 7 per cent. concentration, with the addition of malt extract at the rate of 25 c.c. per 100 c.c. of solution, is only hydrolysed to the extent of about 30 per cent. after 48 hours at 55°.

The products of hydrolysis in this case consisted of almost exactly equal quantities of maltose and dextrose, a fact which was shown, not only by the relation of the optical and the reducing properties of the products, but also by the preparation, separation, and estimation of the osazones.

At first sight, it might be considered that the glucose found in this reaction was a secondary product, the dextrin yielding in the first place maltose, which was subsequently hydrolysed to glucose by the enzymes of the malt-extract. This explanation might certainly apply in those cases where an air-dried malt is employed, for an extract of such a malt often contains a transforming agent which, by long continued action, has an appreciable effect in hydrolysing maltose. In this case, however, a kiln-dried malt was employed whose 'aqueous

extract was shown to be incapable of acting on maltose, even after 60 hours digestion at 55°. We must, therefore, regard the formation of maltose and glucose during the hydrolysis of the dextrin as being simultaneous and not successive phenomena, a fact which, in conjunction with their approximately equal production, is of some importance in its bearing on the constitution of the dextrin.

IX. Generalisations and Conclusions.

When starch is transformed by an active diastase, such as that derived from an air-dried malt, at temperatures below 60° , the reaction proceeds very rapidly until a resting stage is reached corresponding to $[a]_{\rm D}$ 150° and R 80 for the mixed products of change. At this point, these products consist of maltose, and a dextrin which, comparatively speaking, is very resistant to the further action of the hydrolytic agent. This dextrin has a specific rotatory power of $[a]_{\rm D}$ 197—198° and, even when obtained in the purest possible state, has a feeble reducing power corresponding to R 5.5.

Under the mild oxidising influence of mercuric oxide and baryta, the dextrin is converted into a complex carboxylic acid—dextrinic acid.

Under the hydrolytic action of dilute acids; this carboxylic polysaccharide is resolved into d-glucose and a residual C_5 -acid which is identical with the $C_5H_{10}O_6$ -acid obtained either from the acid hydrolysis of the maltodextrinic acids, or from the hydrolysis of the biose acid proceeding from the oxidation of maltose with mercuric oxide.

In the case of maltodextrin and the maltodextrinic acids, on the other hand, the complex is certainly resolvable by diastase into C_{10} -groups only, that is, into maltose.

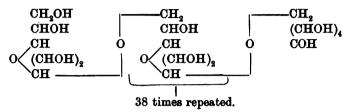
At first sight, this points to there being a difference in the linkings or spatial relations between the C_{12} -groups and their constituent C_6 -groups, and since in the case of dextrin and its derivative dextrinic acid there is no selective disposition on the part of diastase to split off maltose rather than glucose, we are justified in regarding the stable dextrin as made up of C_6 -complexes.

A consideration of all the facts we have brought forward justifies us in regarding the stable dextrin, from an empirical point of view, as a combination of 39 groups of $C_6H_{10}O_5$ - and one $C_6H_{12}O_6$ -group or as $40(C_6H_{10}O_5)+H_2O$.

* In pushing this explanation to its ultimate conclusion, we are, however, met with the difficulty that the diastase of the kiln-dried malt used in these experiments is incapable of hydrolysing maltose. One would expect that a hydrolysing agent which could determine the resolution of the dextrin complex either into C₆-or C₁₂-groups would also be able to resolve any of the fission products into glucose, but this apparently is not the case.

Its constitution may, however, be more rationally regarded as a condensation of 40 glucose molecules with the elimination of the elements of 39 molecules of water.

This constitution may be expressed in the following manner, only one of the 38 similar intermediate groups being represented for the sake of brevity.



On this view, the constitution of dextrinic acid will be given by converting the terminal right hand group to $-CH_2 \cdot [CH \cdot OH]_3 \cdot COOH$, which is the residue of the $C_5H_{10}O_6$ acid given by the complete hydrolysis of dextrinic acid with acids.

These complicated constitutional formulæ can be written in an abbreviated form somewhat similar to that employed for the condensed formula of maltodextrin.

$$\begin{array}{lll} \text{O} \cdot \text{C}_6 \text{H}_{10} \text{O}_4 & \text{O} \cdot \text{C}_6 \text{H}_{10} \text{O}_4. \\ \text{O}_{87} \cdot \left[\text{C}_6 \text{H}_{10} \text{O}_4 \right]_{38} & \text{O}_{87} \cdot \left[\text{C}_6 \text{H}_{10} \text{O}_4 \right]_{38}. \\ \text{O} \cdot \text{C}_6 \text{H}_{10} \text{O}_4 \cdot \vdots & \text{O} \cdot \text{C}_5 \text{H}_{9} \text{O}_5. \\ \text{Stable dextrin.} & \text{Dextrinic acid.} \end{array}$$

The oxygen atoms on the left in each case represent the 39 oxygen linkings between the 40 groups. The sign << is again used to indicate the open carbonyl of the terminal group.

We have now to see how far the above views are in consonance with the observed facts.

It is manifest that an ultimate analysis of such substances cannot determine their exact composition. It would, in fact, be quite impossible by a mere combustion to differentiate a dextrin made up of 39 groups of $C_6H_{10}O_5$ - and one $C_6H_{12}O_6$ -group, from one wholly made up of $C_6H_{10}O_5$ -groups, since the carbon percentages are within 0·12 per cent. It is only by such methods as we have described, that is, by examination of the salts of the derivative acids, and a quantitative study of the products of hydrolysis, that we can expect to have any light thrown on their approximate constitution.

Commencing with the dextrinic acid, the calcium salt of an acid of the above constitution should contain 0.30 per cent. of calcium; the actual amount of calcium found in the pure salt was 0.29 per cent. The amount of glucose which, on the above view, ought to be obtainable from free dextrinic acid by complete hydrolysis is 108.2 per cent., and 107.9 per cent. from its calcium salt. The glucose obtained in our experiments from the free acid was in one case 105.9 per cent., and in another 106.2 per cent., whilst the dry calcium salt of the dextrinic acid gave 107.2 per cent.

Turning now to the acid hydrolysis of the dextrin itself, we note that, with the constitution which we have attributed to it, it ought to yield on complete acid hydrolysis 110.8 per cent. of glucose. The actual amount found by one process was 110.8, and by another 108.9, the error in the second determination being certainly a *minus* one.

We have seen in a previous paper how the cupric-reducing power of the maltose residue of maltodextrin is approximately that of an equivalent quantity of maltose. In the same way, it appears that the glucose residue, constituting the reducing portion of stable dextrin, also retains the reducing power proper to dextrose, for if we regard, as we are entitled to do from the study of its oxidation products, the stable dextrin as constituted of 39 C₆H₁₀O₅ groups and one glucose group, the 'apparent glucose' in this complex, as determined from the actual amount of cupric oxide it reduces, is about 2.7 per cent. This corresponds to an apparent maltose percentage of 5.5, that is, to an R of 5.5, which is exactly the value expressing the reducing power of the dextrin in a pure state.

It now remains to discuss the bearing of our recent work on the size and constitution of the molecule of *starch*, or rather that of *soluble starch*, which differs materially in physical properties from the substance forming the greater part of the starch granule.

The commonly accepted empirical formula for soluble starch, $nC_6H_{10}O_5$, or $nC_{12}H_{20}O_{10}$, is doubtless correct, since it is not only in accord with numerous combustions made from time to time by different observers, but is also fully confirmed by our own work, described in a previous paper (this vol., p. 307), in which we have accurately determined the amount of glucose which it yields under acid hydrolysis, and also the actual amount of products obtained by diastase-hydrolysis.

In our previous writings (Brown and Heron, Brown and Morris, &c.), we have frequently drawn attention to the fact that the quantitative relations of the maltose and dextrin, occurring in starch transformations which have been brought down to the 'resting stage' by diastase, are in close agreement with the view that the reaction takes place according to the empirical equation represented by

$$10C_{12}H_{20}O_{10} + 8H_{2}O = 8C_{12}H_{22}O_{11} + 2C_{12}H_{20}O_{10}.$$

Starch. Maltose. Stable destrin

This is the 'No. 8 equation' of our earlier writings. It assumes VOL. LXXV.

that the dextrin is a substance without cupric-reducing power, and with an empirical formula of $nC_{12}H_{20}O_{10}$ or $nC_6H_{10}O_5$. As we now know that the stable dextrin is not altogether free from reducing power, and that its formula cannot be expressed in a simpler form than by $40C_6H_{10}O_5+H_2O$, the above equation requires modifying in such a manner as to show the interaction of $\frac{1}{10}$ mol. H_2O more than the eight molecules indicated. The multiplication of both sides of the equation by 10, and the introduction of 1 mol. H_2O more, brings the theoretical expression in close accord with the facts: thus

This requires the mixed products of transformation at the close of the reaction to have optical and reducing properties corresponding to $[a]_D$ 149·2°, R 81·8, whilst the old uncorrected expression requires $[a]_D$ 150·2°, R 80·8. The experimental values are always very close to $[a]_D$ 150°, R 80—81.

It must be borne in mind that the value of R 81.8 cannot now be regarded as being quite a measure of the actual amount of maltose present in the products of one of these low transformations, owing to the fact of the dextrin being slightly reducing. The actual amount of free fermentable maltose corresponds to 80.8 per cent., the difference of 1 per cent. being accounted for by the reducing power of the dextrin.

From the quantitative relations of the maltose and dextrin found in the mixed products of starch hydrolysis which have been brought down to the resting stage, it is clear that the size of the starch molecule cannot be less than *five times* that of the stable dextrin.

The study of the dextrinic acid derived from the dextrin has given us a minimum expression of the size of the dextrin molecule, apparently represented by $39(C_6H_{10}O_5),C_6H_{12}O_6$, which indicates a molecular weight of 6498.

In the year 1889 (Trans., 55, 462), one of us, in conjunction with G. H. Morris, described certain attempts which we had made to determine the molecular weight of some of the starch derivatives by means of the freezing-point method, and amongst others we examined the stable dextrin prepared from a starch transformation with diastase run down to the 'resting stage.' This dextrin, prepared by alcoholic precipitation, had optical and reducing properties corresponding to $[a]_D$ 196·2°, R 7·3. Its molecular weight, deduced from the mean of a large number of concordant experiments made on the depression of the freezing point of a strong aqueous solution, was 6221. Although we are less disposed than formerly to base any arguments

on the molecular weight determinations of these colloids by the freezing-point method, it is certainly remarkable that we should have been led to practically the same conclusion as to the molecular weight of the dextrin by considerations entirely independent of each other.

Granted that the molecular weight of the stable dextrin is 6498, the complex representing the molecule of soluble starch cannot have a less molecular weight than 32,400, its empirical formula being represented by $100C_{12}H_{20}O_{10}$ or by $(80C_{12}H_{20}O_{10},40C_6H_{10}O_5)$. The latter expression connotes the fact that the one-fifth of the molecule which gives rise to the stable dextrin on hydrolysis, differs from the remainder which is directly hydrolysable to maltose. The known properties of soluble starch would in themselves suggest a very high molecular weight; its highly colloidal nature, the ease with which it can be removed from its solutions by merely forcing them through porous earthenware, and the extremely small influence it exerts on the freezing point* of its solvent all pointing to a very high molecular complexity, a complexity which probably approaches that of some of the proteids.

Since starch is a non-reducing polysaccharide it does not contain free carbonyl groups.

The simplest manner in which it can be expressed constitutionally, with due regard to all the facts, is to consider it as made up of the residues of 80 maltan groups and 40 dextran groups, linked in ring form through oxygen atoms.

On hydrolysis, the dextran complex, constituting one-fifth of the whole molecule, is split off with the formation of the stable dextrin, $39C_6H_{10}O_5$, $C_6H_{12}O_6$, whilst the maltan portion of the ring is attacked at the oxygen linkings of the C_{12} -groups, the hydrogen ions of the reacting water molecules moving in one direction, and the hydroxyl ions in the other, thus forming, by successive stages of hydrolysis, maltodextrins or "reducing dextrins," \dagger and finally maltose. \dagger

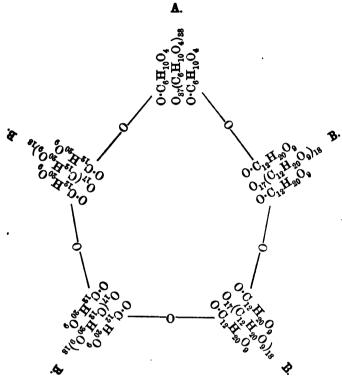
We here give a condensed representation of our views on the constitution of the molecule of soluble starch, A representing the dextran residue, and B the four equal maltan residues. Although in

^{*} We found in 1889 (see Brown and Morris, Trans., 55, 465) that the depression of the freezing point of an aqueous solution of soluble starch was extremely small, indicating a molecular weight between 20,000 and 30,000.

[†] The term mallodextrin is preferable to that of 'reducing dextrin,' since the latter does not connote the all-important fact that such substances do not contain any stable dextrin residue, but are wholly convertible into maltose by diastase hydrolysis.

[†] The manner in which the activity of the diastase has been previously modified by heat, the time of the reaction, and the temperature at which it takes place, are the principal factors in determining the amount of degradation of the maltan portion of the starch.

this condensed constitutional formula we indicate the maltan constituents of the molecule as being arranged in *four* groups, this is not essential to the hypothesis here put forward, for it is possible that the oxygen linkings between the individual C_{12} -groups may all be of



* It will be observed that there are some points of similarity between this constitutional formula for starch and that suggested by Dr. Armstrong in 1880 (see Armstrong's Miller's Elements, p. 658).

the same order, and that the fission due to hydrolysis may occur indifferently at any point of the maltan portion of the chain. The experiments, however, which we described in 1889 (Trans., 55, 469) on the freezing of solutions of high starch products and of transformations arrested at an early stage of hydrolysis, certainly suggest that the early fission products have a molecular complexity about equal to that of the stable dextrin itself; in other words, that the first act of hydrolysis is to divide the starch molecule into five approximately equal parts.

Whilst a consideration of the new facts we have brought forward in these recent papers has led us to very much the same view as that

held by one of us and Morris ten years ago as regards the size and complexity of the starch molecule, our study of the whole question during the last four years has enabled us to substitute for the tentative hypothesis then put forward one which is perhaps a step nearer the truth, and at any rate has the advantage of being more in consonance with the ordinarily accepted views of the constitution of the carbohydrates.

According to the old view, we pictured the starch molecule as consisting of four complex amylin groups arranged round a fifth similar group constituting the portion of the complex which ultimately became the stable dextrin. It was considered that the first action of the diastase was to liberate these five complexes in the form of non-reducing dextrins, and that four of these differed from the fifth in being hydrolysable by successive gradations down to maltose. At that time, the existence of high, degradable, non-reducing dextrins was considered probable, but further investigation has convinced us that such substances do not exist as separate entities, and that all the fission products of starch hydrolysis are, to some extent, reducing, the extent of this reducing power being dependent on the relation of the end carbonyl group to the size of the complex to which it is attached.

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XXXIII.—Position Isomerism and Optical Activity; the Methylic and Ethylic Salts of Benzoyl and of Ortho-, Meta-, and Para-malic Acid.

By PERCY FRANKLAND, Ph.D., F.R.S., and FREDERICK MALCOLM WHARTON, A.I.C., late Priestley Scholar in Mason University College, Birmingham.

THE present investigation forms a continuation of the work on the same subject which we have already published in the pages of the Journal of the Chemical Society (Trans., 1896, 69, 1309—1321; 1583—1592; also P. Frankland and McCrae, Trans., 1898, 73, 307—329) and which has for its object the determination of the influence respectively exerted by position-isomeric groups attached to the asymmetric carbon atom.

Reasons have been adduced by us for anticipating that, in the case of isomeric di-substituted benzene rings, the para-isomeride should exert the greatest, the ortho- the least, and the meta- an intermediate

influence on the rotation, and experiment shows that this sequence is so far, with two doubtful exceptions (Trans., 1898, 73, 308 and 309), uniformly maintained. We have also given reasons for anticipating that the unsubstituted phenyl group should exert a rotatory influence inferior to that of the para- or meta-groups, but according to circumstances either greater or less than that of the ortho-groups. Experience shows, however, that the rotatory influence of the unsubstituted phenyl group is apparently much more erratic, occupying every possible position as regards the magnitude of the rotatory influences of the three isomeric di-substituted benzene rings.

Preparation of Ethylic and Methylic Malates.

The difficulties attending the preparation of the ethereal salts of malic acid have been pointed out by Anschütz and Reitter (Zeit. physikal. Chem., 1895, 16, 493), who have shown that if the ordinary hydrochloric acid method is employed, a considerable proportion of the malic acid is converted into fumaric acid unless a very low temperature is preserved during the saturation of the alcoholic solution of malic acid with hydrogen chloride. It has also been shown by Purdie, Williamson and Lander (Trans., 69, 829; Purdie and Lander, Trans., 73, 287) that if the method of acting on silver malate with an alkyl iodide is employed, the alkyl malate is mixed with the ethereal salt of the corresponding alkoxysuccinic acid which entirely vitiates the optical activity of the product.

In choosing between these two evils, we have resorted to the hydrochloric acid method as the less objectionable of the two, and we have carefully observed the precautions indicated by Anschütz so as to secure the maximum purity of the product.

Ethylic Malate.—Fifty grams of finely powdered malicacid (Kahlbaum), dried in a vacuum desiccator for 3 days, were mixed with 100 grams of absolute ethylic alcohol in which the acid nearly all dissolved; a slow stream of carefully dried hydrogen chloride was then passed through the liquid, which was kept at -18° by means of a freezing mixture. When completely saturated, the liquid was left for 24 hours, a current of dry air was then drawn through for 48 hours, after which it was placed in a vacuum desiccator containing slaked lime, until the smell of hydrochloric acid had nearly disappeared. The excess of alcohol was then distilled off under reduced pressure and at as low a temperature as possible, the ethereal salt being subsequently distilled on an oil-bath. Fifty-one grams of the crude ethereal salt were obtained between 128° and 140° (11 mm. pressure). This exhibited the rotation

 $a_p = -10.30^\circ$; l = 1, $t = 21^\circ$.

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This was redistilled, the portion passing over at 129—134° (12 mm. press.) having a rotation

$$a_{\rm D} = -11.55^{\circ}$$
; $l = 1$, $t = 17.5^{\circ}$.

After treatment in ethereal solution with fused potassium carbonate and redistillation until the rotation was constant, it finally distilled at 129—132° (11 mm. pressure), and exhibited the specific rotation

$$[a]_{0}^{90} = \frac{-11.84}{1.0 \times 1.1340} = -10.44^{\circ}$$
 (d 20°/4° = 1.1340),

a value agreeing closely with that obtained by Purdie and Williamson, namely, -10·30°, from Kahlbaum's malic acid by use of the hydrochloric acid method.

Methylic Molate.—This was prepared in exactly the same way as the ethylic compound. Forty-eight grams of crude ethereal salt, boiling at 128—142° under 12 mm. pressure, were obtained from 50 grams of dry malic acid and 100 grams of methylic alcohol. This product had a rotation

$$a_D = -6.70^\circ$$
; $l = 1$, $t = 18.5^\circ$.

The product was fractionated under diminished pressure until of practically constant rotation; the final product boiled at 129° (11 mm.), and exhibited the following rotations.

$$a_{\rm D} = -8.36^{\circ}$$
; $l = 1$, $t = 16.6^{\circ}$.
 $a_{\rm D} = -8.41$; $l = 1$, $t = 20$
 $a_{\rm D} = -8.46$; $l = 1$, $t = 40$
 $a_{\rm D} = -8.41$
 $a_{\rm D} = -8.41$
 $a_{\rm D} = -8.41$
 $a_{\rm D} = -6.84^{\circ}$.

Purdie and Williamson give as the observed rotation $a_D = -8.17^\circ$. Anschütz and Reitter [a]_D = -6.88° . Walden [a]_D = -6.85° .

Ethylic Benzoylmalate.

Ethylic malate was slowly added to an excess of benzoic chloride heated in an oil-bath at 140°, the temperature being subsequently raised to 170°, at which it was maintained for 40 minutes. The excess of benzoic chloride was distilled off first under reduced pressure and

then, on raising the temperature, the crude ethylic benzoylmalate passed over at 210—220° (12 mm.); the latter was refractionated under diminished pressure until the rotation was constant. It was a thick, colourless liquid which we were unable to obtain in the solid state.

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0.2210 gave 0.4941 CO<sub>2</sub> and 0.1222 H<sub>2</sub>O. C = 60.97; H = 6.14. 0.2153 ,, 0.4818 CO<sub>2</sub> ,, 0.1203 H<sub>2</sub>O. C = 61.03; H = 6.21. C_{15}H_{18}O_6 requires C = 61.22; H = 6.12 per cent. d 40°/4° = 1.1361; d 50°/4° = 1.1253; d 60°/4° = 1.1158.
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With this product, the following polarimetric determinations were made.

Temperature.	Observed rotation and in 99.9 mm. tube.	Density compared with water at 4°.	[α] _D .
21°	- 4·47°	1.1561	- 3·87°
35	-6.02	1.1414	-5.28
46	-7 ⋅00	1.1298	- 6:20
66	-8.59	1.1095	<i>−</i> 7·75
73	-9.02	1.1021	- 8·19
78	-9·31	1.0969	-8:50
98	- 10.57	1.0759	-9.84
137	-12.48	1.0349	- 12:08

Rotation of ethylic benzoylmalats.

Methylic Benzoylmalate.

The mode of preparation was similar to that described above for the ethylic compound. The crude product was dissolved in chloroform, well shaken with a solution of sodium carbonate, and, after separation, the chloroform solution was dried with fused potassium carbonate. After removing the chloroform, the liquid was fractionated under reduced pressure until the rotation was constant, it passed over at 210—223 (12 mm.); it could not be induced to solidify.

The following density determinations were made.

$$d\ 40^{\circ}/4^{\circ} = 1.1944$$
; $d\ 60^{\circ}/4^{\circ} = 1.1759$; $d\ 70^{\circ}/4^{\circ} = 1.1665$, and the following polarimetric observations.

	Rotation	of	methulic	benzor	ulmalate.
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Temperature.	Observed rotation and in 99.9 mm. tube.	Density compared with water at 4°.	[a] _{D.}
21°	-6·81°	1.2121	-5.62°
33	-8.27	1.2009	- 6.89
44	- 9:36	1.1907	- 7 ⋅87
64	- 10.93	$1 \cdot 1721$	- 9:33
99	- 13·16	1.1395	- 11:56
137.5	- 15·04	1.1037	- 13.64

Ethylic Orthotoluylmalate.

This was prepared in the usual manner by adding ethylic malate to twice the theoretical quantity of orthotoluic chloride heated at 140° and ultimately to 170°. The excess of acid chloride was distilled off under reduced pressure, the residue being then dissolved in chloroform and shaken for 24 hours with a solution of sodium carbonate to remove any remaining acid chloride. After washing repeatedly with water, the chloroform solution was dried with potassium carbonate, and the chloroform distilled off. The rotation of the crude product thus obtained was

$$a_D = -5.75^{\circ}$$
; $l = 1$, $t = 20^{\circ}$.

It was purified by repeated fractionation under reduced pressure until the rotation was constant; it distils at 215—225° (12 mm.).

The following density determinations were made,

$$d\ 40^{\circ}/4^{\circ} = 1.1228$$
; $d\ 60^{\circ}/4^{\circ} = 1.1057$; $d\ 70^{\circ}/4^{\circ} = 1.0968$, and the following polarimetric observations.

Rotation of ethylic orthotoluylmalate.

Temperature.	Observed rotation a _D in 92.36 mm. tube.	Density compared with water at 4°.	[a] _{D.}
21°	- 6·58°	1.1391	-6.25°
43	<i>−7</i> ·74	1.1202	<i>-</i> 7·48
71	- 9:04	1.0960	- 8.93
100	-10.27	1.0713	- 10·38
136	- 11·54	1.0403	-12·01

Methylic Orthotoluylmalats.

This was prepared in a similar manner to the ethylic salt. The crude compound, after washing with sodium carbonate solution, exhibited the following rotations.

$$a_{\rm p} = -8.56^{\circ}$$
; $(l=1, t=9.5^{\circ})$
 $a_{\rm p} = -13.08^{\circ}$; $(l=1, t=100^{\circ})$

As solidification could not be induced, the purification was effected by fractionation under reduced pressure until the rotation was constant; the liquid passed over at 214—225° (12 mm.).

The following density determinations were made,

$$d 40^{\circ}/4^{\circ} = 1.1744$$
; $d 50^{\circ}/4^{\circ} = 1.1647$; $d 60^{\circ}/4^{\circ} = 1.1550$,

and the following polarimetric observations.

Rotation of methylic orthotoluylmalate.

Temperature.	Observed rotation a_D in 99.9 mm. tube.	Density compared with water at 4°.	[a] _D .
23°	-10.61°	1.1909	- 8·94°
35.5	-11.17	1.1788	- 9·49
48	-11.72	1.1666	- 10.06
64	-12.45	1.1511	- 10·83
98	-13.85	1.1181	- 12·40
135	- 15.23	1.0822	- 14:09

Ethylic Metatoluylmalate.

The preparation was effected in exactly the same manner as that already described for the orthotoluyl compound. The product was a colourless liquid distilling at 212—220° (13 mm.).

The following density determinations were made,

$$d 40^{\circ}/4^{\circ} = 1.1185$$
; $d 50^{\circ}/4^{\circ} = 1.1086$; $d 60^{\circ}/4^{\circ} = 1.0989$,

and the following polarimetric observations.

Rotation of ethylic metatoluylmalate.

Temperature.	Observed rotation and in 99.9 mm. tube.	Density compared with water at 4°.	[a] _{D.}
21°	- 5·30°	1.1371	-4.67
28	-5. 98	1.1303	- 5:30
33.5	- 6.44	1.1249	- 5.73
38·5	-6.84	1.1200	-6.11
41.5	-7 ·06	1.1170	- 6.33
54 ·5	-7 ·94	1.1043	-7 ⋅20
60	-8.41	1.0989	-7 ·66
71	-9.04	1.0881	-8.32
99.5	-10.52	1.0603	- 9.93
137.5	-11.92	1.0229	- 11.66

Methylic Metatoluylmalats.

This was obtained in like manner, as a thick, almost colourless, liquid distilling at 215—225° (12 mm.).

The following density determinations were made,

$$d \ 40^{\circ}/4^{\circ} = 1.1723$$
; $d \ 50^{\circ}/14^{\circ} = 1.1622$; $d \ 60^{\circ}/4^{\circ} = 1.1521$, and the following polarimetric observations.

Rotation of methylic metatoluylmalate.

Temperature.	Observed rotation and in 99.9 mm. tube.	Density compared with water at 4°.	[a] _D
20°	- 7·55°	1.1925	- 6·34°
32	- 8.68	1.1804	-7:36
46	- 9.85	1.1662	- 8· 45
67.5	- 11:31	1.1445	- 9.89
99	- 13:04	1.1127	- 11·73
136	- 14·49	1.0753	13 · 4 9

Ethylic Paratoluylmalats.

The preparation was carried out in exactly the same manner as already described for the orthotoluyl compound. The ethylic salt was obtained as a thick, colourless liquid which was purified by fractionation under reduced pressure until the rotation was constant.

The following density determinatations were made,

 $d~40^{\circ}/4^{\circ}=1.1162$; $d~50^{\circ}/4^{\circ}=1.1052$; $d~60^{\circ}/4^{\circ}=1.0943$, and the following polarimetric observations.

Rotation of ethylic paratoluylmalate.

Temperature.	Observed rotation α_D in 99.9 mm. tube. -0.25°	Density compared with water at 4°. 1.1382	[a] _{D.} - 0.22°
29	- 1.06	1.1283	-0.94
35	_ 1·71	1.1217	- 1·53
51	- 2 ·99	1.1041	-2.71
62	- 3.71	1.0920	- 3.40
99	- 5.83	1.0513	- 5.55
136	-7:38	1.0106	-7·31

Note.—On the first occasion when we prepared ethylic paratoluyl-malate, this substance, before distillation, but after it had been washed in chloroform solution with sodium carbonate, became quite thick through separation of crystals; the latter were recrystallised several times from methylated spirit until of constant melting point (95°), when they presented the appearance of long, shining blades. These crystals dissolved slowly in caustic potash on heating, and on adding hydrochloric acid, paratoluic acid melting at 176° was deposited. On analysis,

$$0.1549$$
 gave 0.4257 CO₂ and 0.0787 H₂O. C= 74.95 ; H= 5.65 . 0.1812 , 0.4990 CO₂ , 0.0919 H₂O. C= 75.11 ; H= 5.64 .

These figures negatived the possibility of this substance being ethylic paratoluylmals e, but, on the other hand, they point unmistakably to its being aratoluic anhydride, $C_{16}H_{14}O_{3}$, which requires C=75.60, H=5.51 p.r. cent. As this compound does not appear to have been prepared before, we had no further means of identifying it with the quantity at our disposal. Benzoic anhydride melts at 42° .

Methylic Paratoluylmalate.

Even this ethereal salt was only obtained as a liquid distilling between 200° and 225° under 13 mm. pressure.

The following density determinations were made,

 $d\ 40^{\circ}/4^{\circ} = 1\cdot1725$; $d\ 50^{\circ}/4^{\circ} = 1\cdot1617$; $d\ 60^{\circ}/4^{\circ} = 1\cdot1509$, and the following polarimetric observations.

Rotation of methylic paratoluylmalate.

Temperature.	Observed rotation a _D in 99 9 mm. tube.	Density compared with water at 4°.	[a] _{D.}
18·5°	- 3·75°	1.1957	- 3·14°
29.5	- 4·77	1.1838	- 4.03
37.5	- 5.40	1.1752	- 4.60
50	- 6·35	1.1617	- 5·47
66	-7.40	1.1444	- 6.47
99	- 9·23	1.1088	- 8:33
136	- 10.83	1.0688	-10.14

The results recorded above may be summarised as follows.

- 1. The laworotation of ethylic is greater than that of methylic malate.
- 2. The lævorotation of ethylic malate is diminished by the introduction of the benzoyl and three toluyl groups. The lævorotation of methylic malate is also diminished by the introduction of the benzoyl, paratoluyl, and metatoluyl groups, but is increased by the introduction of the orthotoluyl group. The exceptional influence of the orthotoluyl group on methylic malate will be discussed later, the uniform effect in the other cases of the substitution is to depress the lævorotation, or, in other words, to exert a dextrorotatory, influence.
- 3. At the ordinary temperature (20°), the dextrorotatory influence of these groups follows in the order

paratoluyl > benzoyl > metatoluyl > orthotoluyl both for methylic and ethylic malate.

4. At a high temperature (136°), on the other hand, the sequence of the dextrorotatory influences of these groups is

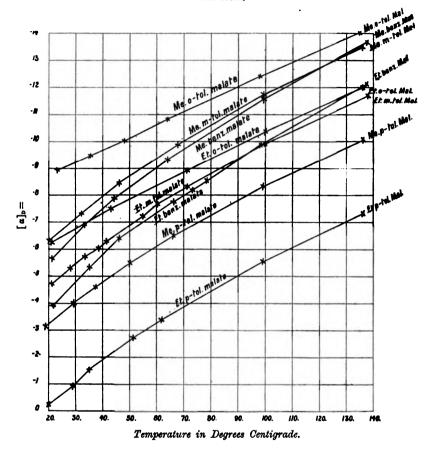
paratoluyl > metatoluyl > benzoyl > orthotoluyl in the case of methylic malate, and

 $paratoluyl > metatoluyl > \begin{cases} orthotoluyl \\ benzoyl \end{cases} \begin{cases} which are practical in the case of ethylic malate. \end{cases}$

Thus it will be seen from the diagram on p. 346 that the specific rotation curve for methylic benzoylmalate cuts that for methylic metatoluylmalate at a temperature of about 120°, and that the specific rotation curve for ethylic benzoylmalate cuts that for ethylic metatoluylmalate at about 95°, and that for ethylic orthotoluylmalate at about 132°. Again, it will be seen that the influences of the benzoyl, metatoluyl, and orthotoluyl groups become almost identical at the high

Specific Rotation of Methylic and Ethylic Salts of Benzoyl and Toluyl (o, m, and p)

Malic Acid,



temperature (136°), both in the case of ethylic and methylic malate respectively.

5. At the ordinary temperature (20°), the rotatory influences of the several groups are as follows.

	Methylic malate	dextrorotatory
Benzoyl <		٨
	Ethylic malate	ditto.
	Methylic malate	lævorotatory
Orthotoluyl -	{ · ·	•
_	Ethylic malate	dextrorotatory.
	(Methylic malate	dextrorotatory
Metatoluyl -	{	۸
•	Ethylic malate	ditto.

 $\begin{array}{cccc} \textbf{Paratoluyl} & \left\{ \begin{array}{ccc} \textbf{Methylic malate} & & \textbf{dextrorotatory} \\ & & & \land \\ \textbf{Ethylic malate} & & \textbf{ditto.} \end{array} \right. \end{array}$

Thus in all cases the dextrorotatory influence of the aromatic group is greater on the ethylic than on the methylic compound, indeed the orthotoluyl group, whilst exerting a dextrorotatory influence on ethylic malate, exerts a levorotatory influence on methylic malate.

6. At a high temperature (136°), on the other hand, the rotatory influences of the several groups are as follows.

_	(Methylic malate	lævorotatory
Benzoyl	Ethylic malate	∨ ditto.
Orthotoluyl	Methylic malate	lævorotatory
0101010111	Ethylic malate	ditto.
Metatoluyl	Methylic malate	lævorotatory V
	Ethylic malate	ditto.
Donatalani	Methylic malate	lævorotatory
Paratoluyl	Ethylic malate	dextrorotatory.

Thus, again, the dextrorotatory influence of the aromatic group is more pronounced on the ethylic than on the methylic compound; indeed, at the high temperature the influence of all four aromatic groups is actually levorotatory on methylic malate, whilst the paratoluyl group at any rate has still a dextrorotatory influence on ethylic malate.

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XXXIV.—Some Regularities in the Rotatory Power of Homologous Series of Optically Active Compounds.

By PERCY FRANKLAND, Ph.D., F.R.S.

It is difficult to find a consistent explanation for the phenomena to which attention has been drawn in the preceding paper, the lower laworotation of the substituted ethylic malates being particularly perplexing when it is borne in mind that the laworotation of methylic malate is lower than that of ethylic malate. Thus it would be anticipated that the dextrorotatory influence of the aromatic acidyl group should depress the laworotation of both methylic and ethylic malates, and that the methyl compound should have a smaller laworotation of both methylic and ethylic malates, and that the methyl compound should have

rotation than the ethyl compound, whilst, as a matter of fact, the reverse is actually the case.

The following explanation is provisionally suggested to account for the facts.

The experimental specific rotations of methylic and ethylic malates are not the specific rotations of monomolecular bodies; both of these ethereal salts are associated, and the methyl compound is more highly associated than the ethyl compound. This association leads to a lower negative specific rotation than is possessed by the monomolecular substances, and of the latter the methylic has a higher negative rotation than the ethylic.

On introducing the acid radicles, the molecules become simple or more nearly so, and the dextrorotatory influence which they exercise depresses the negative rotation of both methylic and ethylic malate, the negative rotation of the methylic naturally remaining greater than that of the ethylic compound.

This explanation is also in general harmony with the results obtained by Walden (*Zeit. physikal. Chem.*, 1895, 17, 245—266) in the case of other derivatives of malic acid. Thus,

[a]30°	[a]90°
Dicaprylic ,,	6.92 (about)
Diamylic ,,	9.92
Di-isobutylic ,,	11.14
Di-isopropylic,,	10.41 (about)
Dipropylic ,,	11.62
Diethylic ,,	10·18
Dimethylic malate	-6.85°
	[α] _D ²⁰

		[a] _{20°}		[a] ^D °°		[a]20°
Dimethylic ace	tylmalate	- 22°92°	propionylmalate	- 22.94°	butyrylmalate	- 22·44°
Diethylic	,,	- 22.52	,,	-22.20	,,	- 22 22
Dipropylic	,,	-22.85			,,	- 22.40
Di-isobutylic	,,	- 21 ·88				- 21 ·68

		[a] _{20°}		[a] _D
Dimethylic iso	butyrylmalate	- 22·36°	isovalerylmalate	- 22·89°
Diethylic	,,	- 21 ·99	,,	- 22:07
Dipropylic	,,		,,	-21.68
Di-isobutylic	,,		**	- 19 91
Dimethylic bro	macetylmalate	- 22:40	chlorosuccinate	+41.42 *
Diethylic	,,	- 22·48	,,	+27.50
Dipropylic	,,	- 22:24	,,	+25.68
Di-isobutylic	,,	 20 · 38	,,	+21.57
Diamylic	,,		,,	+21.56

^{*} Walden has shown that the chlorosuccinates really corresponding with the ordinary malates have the same involvations (Ber., 1896, 29, 138).

In the case of all these substituted malates, the substitution raises the levorotation, and in each substituted series, excepting that of bromacetylmalic acid, the methylic has a higher rotation than the ethylic compound.

The following evidence of the association or otherwise of the several compounds referred to in the previous paper is afforded by Traube's formula for the calculation of molecular volume.*

				Calculated mol. vol. at 15°.	Mol. wt. d15°/4°	Experimental mol. vol. at 15°.
Meth y lio	malate .			140.6	162 1.2851	131.2
,,	benzoyln	nalate	•••••	215.6	$\frac{266}{1\cdot2175}$	218.5
,,	ortho-tol	luylmala	te	231.7	280 1·1986	233.6
,,	meta-	,,		,,	280 1·1975	233.8
,,	para-	,,	•••	,,	280 1·1995	233·4

^{*} The calculated molecular volumes given in this paper have been obtained by using the formula $V_m = m9.9C + n3.1H + p2.3O' + q5.5O'' + 25.9$, in which O' = atomic volume of hydroxylic oxygen. The value for O' becomes 0.4 when OH is attached to a carbon atom which is also doubly linked to an atom of oxygen (carboxyl group) or when the neighbouring carbon atom is also attached to an OH-group, as in the ethereal salts of tartaric acid. O'' = atomic volume of oxygen when doubly linked to carbon (either to one or to two carbon atoms). 25.9 = ``Covolume.'' 13.2 is deducted for each benzene ring present in the molecule (Ber., 1895, 28, 2724).

In my paper in conjunction with Dr. McCrae (Trans., 1898, 78, 324), on some of the monacidyl derivatives of ethylic tartrate, the values employed were taken from an earlier communication of Traube's, and these led to a wider divergence between the calculated and experimental molecular volumes than when the above more recent figures are used in calculation. Thus

•		Calculated mol. vol. at 15°.		Experimental mol. vol.
		Former.	Present.	at 15°.
Ethylic	monobenzoyltartrate	248.8	252·8	255.6
,,	monopara-toluyltartrate	264.9	268.4	275.4
,,	monometa- ,,	,,	,,	274.7
,,	monortho- ,,	,,	,,	271.5
,,	dibenzoyltartrate	327-2	342.7	344. 5
,,	dipara-toluyltartrate	859·4	874.9	879.6
19	dimeta- ,,	,,	,,	879.0
**	diortho- ,,	,,	,,	878·9
Methylic	dibenzoyltartrate	295.0	310.5	307.5
,,	dipara-toluyltartrate	827.2	842.7	841.4
12	dimeta- ,,	,,	,,	841.7
,,	diortho- ,,	,,	,,	335·8
Methylic		138-2	139.1	188.5
Ethylic	,,	170.4	17178 tiz	ed by 1701 09[6
VOI. I.Y	(V			A A

				Calculated mol. vol. at 15°.	Mol. wt. d15°/4°	Experimental mol. vol. at 15°.
Ethylic	malate	••••••	•••••	172.8	190 1·1890	166.8
**	benzoylm	alate	•••••	247.8	294 1·1631	252.8
**	ortho-tolu	ylmalate	•••	263 9	808 1·1442	269 2
**	meta-	**	•	**	$\frac{308}{1\cdot 1432}$	269•4
**	para-	" .		"	808 1·1487	269 3

From these figures, it appears that both ethylic and methylic malate are associated, and the latter much more strongly than the former, whilst the aromatic acidylmalates are not associated, their experimental molecular volumes being, indeed, in excess of the calculated values. This being the case, it is not improbable that the laworotation of unassociated methylic malate may be greater than the laworotation of unassociated ethylic malate, and, in fact, that the real values of $[a]_D$ for the monomolecular ethereal salts of malic acid diminish in passing up the series, from the methylic term. This view is borne out by applying Traube's formula to the known members of the series as prepared and examined by Walden (loc. cit.). It should be noted that Walden's densities were all determined at 20°, so that the experimental molecular volumes for that temperature are a little-higher than they would be for 15°, but the difference is too small to render recalculation worth while at this stage of the inquiry.

	Calculated mol. vol. at. 15°.	Mol. wt. d20°/4°	Experimental mol. vol. at 20°.
Dimethylic malate	140.6	162 1·2337	181.8
Diethylic ,,	172.8	$\frac{190}{1.1294}$	168 -2
Dipropylic ,,	205.0	218 1:0745	202-9
Di-isopropylic malate	205.0	218 1.0760	202.6
Di-isobutylic ,,	237-2	246 1.0418	236.1
Diamylic ,,	269 • 4	274 1·0790 (1)	[258-9] *
Dicaprylic ,,	866.0	358 0·9761	866.8

The above figures show that, in ascending the series, the terms exhibit less and less evidence of association; indeed, the experi-

^{*} There can be little doubt that this figure is incorrect, through the density (1 079) being wrongly given in Walden's paper. The density should obviously lie between those of the butylic and caprylic compounds.

mental molecular volume of dicaprylic malate is somewhat in excess of the calculated.

The ethereal salts of malic acid are generally cited as an instance of an homologous series exhibiting a 'maximum rotation' (Guye and Chavanne, Bull. Soc. Chim., 1896, [iii], 15, 190), and, as is well known, these maxima occurring in homologous series have been used by Guye to support his views concerning the "product of asymmetry." In the present instance, however, the maximum exhibited in the series of ethereal salts of malic acid is explicable on the very probable assumption, based on molecular volume, of association occurring in a diminishing degree from the methylic compound upwards. Moreover, the product of asymmetry does not predict a maximum rotation within this series, but, on the contrary, demands that the rotations should continuously diminish in ascending the series, thus,

		Produ	act of asymmetry. $P \times 10^6$.
Dimethylic	malate		-193
Diethylic	,,	.,	-171
Dipropylic	"		-148
Dibutylic	,,		-128
Diamylic	"		-111
Dicaprylic	"	••••	75

From the following tables, it will be seen that, according to Traube's formula, the substituted malates described by Walden are either not associated at all, or only slightly so, even in the case of the methylic compound.

Ethereal salts of acetylmalic acid. (Walden, loc. c

	Density 20°/4°.	[a] _p .	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. exp. for 20°.
Dimethylic	1·1975	- 22 ·92°	0	175°3	170·3
Diethylic	1·1168	- 22 ·52	- 22	207°5	207·7
Dipropylic	1·0724	- 22 ·85	- 35	289°7	242·4
Di-isobutylic	1·0362	- 21 ·88	- 49	271°9	277·9

Ethereal salts of propionylmalic acid. (Walden, loc. cit.)

Dimethylic	1·1609 1·0958 —	- 22·94° - 22·20 	0 0 -10 -23	191·4 223·6 —	187·8 224·5 —
!		ł · !		Digitized by	Gogle

	Density 20°/4°.	[a] _≥ .	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. exp. for 20°.		
Ethereal s	alts of bu	tyrylmalio	acid. (We	lden, <i>loc</i> .	oit.)		
Dimethylic	1·1817 1·0786 1·0417 1·0146	- 22·44° - 22·22 - 22·40 - 21·68	-17 0 0 -7	207·5 239·7 271·9 804·1	205·0 242·2 276·5 811·4		
Ethereal sai	ts of isob	utyrylmal	ic acid. (W	alden, loc	. cit.)		
DimethylicDiethylic	1·1255 1·0688	- 22:86° - 21:99	- 17 0	207·5 289·7	206·1 248·3		
Ethereal sai	lts of is ov	alerylmali	c acid. (W	alden, <i>loc</i> .	cit.)		
Dimethylic	1·1034 1·0605 1·0263 1·0045	-22.89° -22.07 -21.68 -19.91	-42 -10 0 0	223 ·6 255 ·8 288 ·0 320 ·2	222·9 258·4 294·3 828·5		
Ethereal salts of bromacetylmalic acid. (Walden, loc. cit.)							
Dimethylic	1·5072 1·3986 1·3150 1·2022	- 22·40° - 22·48 - 22·24 - 20·38	-104 -55 -25 -9	189·9 222·1 254·3 286·5	187·8 223·2 257·8 805·3		
Ethereal sa	lts of chl	orosuccinic	o acid. (We	alden, <i>loc</i> .	cit.)		
Dimethylic	1·2555 1·1498 1·0925 1·0524 1·0819	+41.42° +27.50 +25.63 +21.57 +21.56	-78 -100 -109 -111 -107	148·4 180·6 212·8 245·0 277·2	148-8 181-4 216-5 251-8 283-5		

The phenomena in the case of the chlorosuccinates would appear to admit of twofold interpretation: either the normal rotation of dimethylic chlorosuccinate is so much in excess of that of the ethylic compound that the association of the methyl compound does not depress its rotation below that of the ethylic chlorosuccinate, or the association actually leads in this case to an increase of dextrorotation.

The two series of the ethereal salts of methoxy- and ethoxy-succinic acids may also be regarded as substituted malates and considered along with the preceding ones; for these, the following data have been obtained by Purdie and Williamson (Trans., 1895, 67, 971).

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	Product of asymmetry $P \times 10^6$.		Mol. vol. experimental.
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Ethereal salts of methoxysuccinic cid.

	[1	1 170
Methylic	+52.51° (at 12°)	-106	159.9	$\frac{176}{1.1498} = 153.1 \text{ (for } 12^{\circ}\text{)}$
Ethylic	+50-11 (at 18°)	- 122	192·1	$\frac{204}{1.0705}$ = 190.6 (for 18°)
Propylic	+45°21 (at 15°)	- 125	224 · 8	$\frac{282}{1.0419} = 222.7 \text{ (for 15°)}$
Butylic (norm.)	+41.68 (at 15°)	-121	256.5	$\frac{260}{1.0149} = 256.2 \text{ (for 15°)}$

Ethereal salts of ethoxysuccinic acid.

	1		ŀ	1
Methylic	+59.86° (at 18°)	- 32	176.0	$\frac{190}{1 \cdot 1055} = 171.9 \text{ (for 13°)}$
Ethylic	+55.29 (at 17°)	- 59	208·2	$\frac{218}{1.0418} = 209.2 \text{ (for 17°)}$
Propylic	+51.81 (at 15°)	-76	240 · 4	$\frac{246}{1.0131} = 242.8 \text{ (for 15°)}$
Butylic (norm.)	+46.48 (at 6°)	- 85	272.6	$\frac{274}{0.9978}$ = 274.7(for 15°)

^{*} The density is only given for 6° (1.0045), the value for 15° has been calculated on the assumption that the density diminishes by 0.0008 for each 1° rise in temperature.

These two series are particularly interesting; they each exhibit continuously diminishing rotations, whilst the product of asymmetry predicts a maximum at the propylic term for the first, and a maximum for a higher term in the case of the second series. In each series, the methylic term alone furnishes much evidence of association, but in neither series does this association lead to the methylic compound having a lower rotation than the ethylic. However, in each series the rotation of the methylic compound is anomalous, thus the difference in rotation between the methylic and ethylic methoxysuccinate is less than between the other consecutive terms of the series, whilst the difference in the case of the methylic and ethylic ethoxysuccinate is greater than that between the next two consecutive terms of this series Moreover, the methylic compound with the most anomalous rotation has also the most anomalous molecular volume.

Thus this very justifiable assumption with regard to the association and consequent masked rotation of the initial terms of the series of unsubstituted malates is in general harmony with the fact that in the

several series of substituted malates the methylic compound has almost without exception the highest levorotation.

The question next arises as to whether those homologous series in which the product of asymmetry demands a maximum rotation, and in which a maximum actually occurs, also exhibit this phenomenon of association in the initial terms.

Of series exhibiting such a maximum rotation approximately in harmony with the demands of the product of asymmetry, one of the first to be prepared and most fully investigated is that of the ethereal salts of glyceric acid, thus (P. Frankland and MacGregor, Trans, 1893, 63, 511 and 1410; P. Frankland and Price, Trans, 1897, 71, 253).

			, g-g-11-11-11-		
	Density 15°/15°.	[a] ¹⁵ °.	Product of asymmetry $P \times 10^6$.	Mol. vol. calculated for 15°.	Mol. vol. at 15° experimental.
Methylic Ethylic	1·2798 1·1921	- 4 ·80° - 9 ·18	+288·8 +344·8	102·1 118·2	93·8 112·4
Propylic	1.1808	- 12:94 - 11:82 - 13:19	+ 358·2 + 358·2 + 346·8	134·3 184·3 150·4	129·8 130·9 146 · 2
Butylic (norm.) Isobutylic Amylic (secondary	1.1051	- 14·23	+346.8	150.4	146.6
butylmethyl) Heptylic (norm.)	1.0786 1.0890	-14·12 -11·80	+324·3 +268·7	166·5 198·7	163·2 196·3
Octylic (norm.)	1.0263	-10.22	+241.8	214.8	212.4

Ethereal salts of glyceric acid.

Thus all the known terms of this series exhibit association, the latter being most pronounced, as before, in the case of the lower members, and becoming less and less marked as the series is ascended. If it be assumed that this association depresses the rotation, it obviously becomes highly doubtful whether the maximum rotation, which the series exhibits, has any real connection with the maximum indicated by the products of asymmetry.

Again, another homologous series which has been very fully investigated is that of the ethereal salts of diacetylglyceric acid; it exhibits a very marked maximum rotation, but at a term very far removed from that predicted by the product of asymmetry. The following (next page) are the values which have been found (P. Frankland and MacGregor, Trans., 1894, 65, 750; P. Frankland and Price, loc. cit.).

This series is peculiarly instructive, as it shows how unconnected is the phenomenon of maximum rotation with the maximum product of asymmetry. Thus, whilst the maximum rotation falls on the isobutyl term (as in the series of glycerates), the maximum product of asymmetry is not reached until the term C₁₃H₂₇. There is also much less

Ethereal salts of diaces	ŊŲ	glyd	erio	acid.
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	Density 15°/15°.	[a] _p ¹⁵ .	Product of asymmetry $P \times 10^6$.	Mol. vol. calculated for 15°.	Mol. vol. at 15° experimental.
Methylic	1·1998 1·1574 1·1268 1·1198	-12.04° -16.31 -19.47 -17.97	0 0 +17.4 +17.4	175·8 191·4 207·5 207·5	170 · 0 188 · 4 206 · 0 207 · 8
Isobutylic	1·0990 1·0824	-20.48 -19.44 -16.68 -15.87	+41.9 +67.8 +110.4 +126.2	223·6 239·7 271·9 288·0	228·8 240·2 278·3 290·2

evidence of association in the case of the methylic compound than in the case of the glycerates, and coincidentally with this the rotations of the initial terms of the diacetylglyceric series are less markedly inferior to the maximum rotation than in the glyceric series.

	Density.	[a] _{b.}	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. experimental.
72.7		77 . 7	,	/10 17	

Ethereal salts of dimonochloracetylglyceric acid. (P. Frankland and Patterson, Trans., 1898, 73, 181.)

Ethylic	1.3693 (15°)	- 12·91° (15°) - 16·80 (15°)	+42 +16	195·5 211·6	191 ·4 (15°) 209 ·6 (15°)
Propylic	_	l —	+8		
Butylic		-	-1		-
		1		ļ.	

Ethereal salts of di-dichloracetylglyceric acid. (P. Frankland and Patterson, loc. cit.)

Ethylic 1·4667(16·8°) - 18·33 (16·8°) - 4 Propylic	+ 64 215·7 + 85 231·8 + 28 —	228·7 (15°) 242·7 (16·8°) —
-------------------------------------------------------	------------------------------------	-----------------------------------

Ethereal salts of di-trichloracetylglyceric acid. (P. Frankland and Patterson, loc. cit.)

Ethylic 1.5502 (12°) - 18.66 (12.5°) + 58 252.0 274.1 (12°) Propylic + 38

In the above three series, the relations are essentially similar to those found in the diacetylglycerates; there is only evidence of association in the case of the dimonochloracetylglycerates, and in all cases the methylic compound has a distinctly lower rotation than the ethylic. The levorotation of the methylic and ethylic glycerates is, in fact, simply augmented by a certain number of degrees in each case.

It will be noticed that the molecular volumes calculated by Traube's formula generally fall very far short of the experimental values in the case of these chlorine compounds. This abnormally large molecular volume of compounds containing much chlorine has already been pointed out by Traube.

Another very similar series is that of the ethereal salts of dibenzoylglyceric acid, of which several terms have been prepared and studied (P. Frankland and MacGregor, Trans., 1896, 69, 104; P. Frankland and Price, Trans., loc. cit.).

	Density 15°/4°.	[a] ₁₈ ,	Product of asymmetry $P \times 10^6$.	Mol. vol. calculated for 15°.	Mol. vol. at 15° experimental.
Methylic Ethylic	1 ·2211 1 ·2010	+ 26 · 89° + 26 · 58	+61.8° +87.4	273·5 289·6	268·6 284·8
Propylic	1.1807	+21.00	+19.1	305.7	801.2
Amylic (secondary butylmethyl)	1.1461	+18:31	+1.2	887 -9	885.0

Ethereal salts of dibenzoylglyceric acid.

There is thus evidence of association throughout the known terms of the series. In this series, the product of asymmetry reaches a minimum at the hexylic term, after which it again increases, the rotations diminish from the methylic term upwards, but the rotation of the methylic term is distinctly anomalous, the difference between it and the ethylic being much smaller than that between the ethylic and propylic terms. Presumably, the normal rotation of all the members of this series is higher than that given above, the rotation of the methylic compound being the greatest; indeed, it has been shown (P. Frankland and Pickard, 1896, 69, 123) that in glacial acetic acid (in which fairly normal molecular weights were obtained by the cryoscopic method) the rotation of methylic dibenzoylglycerate ranged from $[a]_D = +32.38^{\circ}$ (c=18.6 per cent.) to $+34.34^{\circ}$ (c=1.7 per cent.), whilst in benzene solution (in which the molecular weights were distinctly below the theoretical) the rotation ranged from $[a]_{D} = +40.72^{\circ} (c = 34.1 \text{ per cent.}) \text{ to } +45.70^{\circ} (c = 3.0 \text{ per cent.}).$

Ethereal salts of lactic acid. (Walker, Trans., 1895, 67, 916.)

	Density.	[a] _{D.}	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. experimental.
Methylic	1·100 (13°/4°)	- 11·1°	- 79	103.6	94.5 (13°)
Ethylic	1·080 (19°/4°)	- 14·52	- 74	119.7	114.6 (19°)
Propylic	1·004 (19°/4°)	- 17·06	- 65	185.8	181.5 (19°)

Ethereal salts of acetyllactic acid. (P. Frankland and Henderson, Proc., 1895, 54.)

Rthylic* 1.0527 (15°/15°) -41.47 -199 154.4 152.0 (15°)	Methylic* 1.0957 (15°/15' Ethylic* 1.0527 (15°/15'	-43·41° -41·47	0 - 199		138·2 (15°) 152·0 (15°)
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Ethereal salts of chloropropionic acid. (Walker, Trans., loc. cit.)

Methylic 1: Ethylic 1: Propylic 1:	l ·0821 (15°/4°)	+19.88	- 326 - 417 - 447	111·4 127·5 148·6	107·1 (15°) 126·1 (15°) 143·0 (15°)
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Ethereal salts of bromopropionic acid. (Walker, loc. cit.)

Methylic	1·482 (17°/4°)	+42.65°	+278	131.8	112·7 (17°)
Ethylic	1·386 (19°/4°)	+31.45	+90		130·6 (19°)
Propylic	1·315 (14°/4°)	+21.98	-88		148·3 (14°)

^{*} The lactic acid from which these compounds were prepared was afterwards found to be partially racemised, so that the absolute values given for the rotations are, of course, too small, but the ratio between the two is probably correct.

N.B.—It has been shown by Purdie and Williamson (Trans., 1896, 69, 837) that the change of sign in the case of the chloro-and bromo-propionates is due to inversion, as in the case of the chloro-succinates from malic acid.

The relations exhibited by the series of lactates and acetyllactates are very similar to those already drawn attention to in the case of the malates and acidylmalates. Thus the rotation of methylic lactate is less than that of ethylic lactate, whilst methylic acetyllactate has a higher rotation than ethylic acetyllactate. The lower rotation of methylic than of ethylic lactate, it will be observed, is coincident with a much greater degree of association of the methylic than of the ethylic compound, whilst the amount of association in the case of the acetyllactates is not nearly so great. It may, therefore, be inferred

that in the acetyllactates the association of the methylic compound is not sufficient to depress its rotation below that of the ethylic compound. The phenomena in the case of the chloro- and bromopropionates are similar to those exhibited by the acetyllactates.

There are two homologous series of active compounds to which great prominence has been given by Guye as supporting the connection between maximum product of asymmetry and maximum rotation; these are the ethereal salts of active amylic alcohol and of active valeric acid respectively. The data given in the two following tables have been furnished by the investigations of Guye and Chavanne (Bull. Soc. Chim., 1896, [iii], 15, 177, 273).

Ethereal salts of active amylic alcohol. (Guye and Chavanne, loc. cit.)

	Density.	[a] _P	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. exp.
,, formate, ,, acetate, ,, propionate	0.860 (20°) 0.861 (20°) 0.871 (20°) 0.859 (20°) 0.854 (20°)	+2·01 +2·53 +2·77 +2·69 +2·52 +2·40 +2·21 +2·10 +1·95 +1·88 +1·56 +1·28	27 382 374 372 851 321 289 258 229 204 144 93·5 76·7	114·9 188·5 149·6 165·7 181·8 197·9 214·0 230·1 246·2 262·3 294·5 310·6 375·0 407·2	106·8 (11°) 131·5 (20°) 149·0 (20°) 165·6 (20°) 183·8 (20°) 200·0 (20°) 216·5 (20°) 232·8 (20°) 248·8 (20°) 264·8 (20°) 293·9 (20°) 314·3 (20°) 381·7 (20°) 414·0 (20°)

In this series, therefore, the product of asymmetry attains a maximum at the acetate term, whilst the maximum dextrorotation is actually exhibited by the following, or propionate, term. On comparing the calculated and experimental molecular volumes, it will be seen that the first few terms are tainted with the evidence of association, and it is highly probable that the rotations which they exhibit are not those of the single molecules. Thinking that possibly the lævorotation of amylic alcohol itself might be due to association, and that the single molecule was perhaps dextrorotatory like the other terms of the series, I have had its rotation determined in alcoholic solution by Mr. Mason, B.Sc., with the result that a more highly lævorotatory figure was obtained. As the amylic alcohol would presumably be less associated in alcoholic solution than in the

pure state, it may be inferred that monomolecular amylic alcohol has a higher levorotation than $[a]_0 = -4.62.$ In this case, then, the above series starts with a levorotation, which becomes diminished by successive additions to the variable group until the propionate term of the series is reached, beyond which further additions to the variable group slowly increase the levorotation, or, rather, diminish the dextrorotation. Regarded in this light, the series is levorotatory, its ascent being attended by diminution of the levorotation, a minimum levorotation being reached at the propionate term. This is, as far as I am aware, the only series in which a minimum has actually been discovered (see, in this connection, p. 369).

Ethereal salts of active valeric acid. (Guye and Chavanne.)

	Density.	[a] _D .	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. experimental.
Valeric acid	0·938 (22°)	+18.64° (in liquid state) +17.3° (in aqueous	218	114.0	108·7 (22°)
Methylic valerate Ethylic ,, Propylic ,, Butylic ,, Isobutylic ,, Benzylic ,,	0.864 (22°) 0.860 (22°) 0.856 (22°) 0.855 (22°)	+18.44	882 <i>\$74</i> 878 851 - 851 221	188.5 149.6 165.7 181.8 181.8 192.1	181·5 (22°) 150·5 (22°) 167·4 (22°) 184·6 (22°) 184·8 (22°) 195·5 (22°)

This series exhibits very similar relations to those discussed above for the ethereal salts of active amylic alcohol. The product of asymmetry attains a maximum for ethylic valerate, whilst the maximum rotation is actually found in the case of methylic valerate, that is, for the term just preceding that which the product of asymmetry predicts. It will, however, be observed that the rotation of methylic is very much in excess of that of ethylic valerate, so that, apparently, the slight association, of which there is evidence in the case of methylic valerate, is not sufficient to absolutely depress its rotation below that of ethylic valerate. In the case of liquid valeric acid itself, however, there is evidence of much greater association than for methylic valerate, and probably this degree of association is sufficient to depress

^{*} It has, further, been quite recently shown by Guye and Emily Aston (Abstr., 1898, ii, 469) that amylic alcohol in aqueous solution gives a value $[\alpha]_D = -5.1^\circ$, whilst in benzene solution it is $[\alpha]_D = -4.5$, thus corroborating the above assumption as to the higher levorotation of unassociated amylic alcohol.

the rotation of valeric acid below that of the methylic compound. This interpretation is, to some extent, borne out by the fact that aqueous valeric acid has actually a higher rotation than methylic valerate, although the rotation may in this case be complicated by the circumstance that, in aqueous solution, the valeric acid is partially ionised.

Another series cited by M. Guye (loc. oit.) as furnishing a verification of the predictions of the product of asymmetry is that of the active amylic oxides, the data for which are contained in the following table.

Active amylic oxides. (Guye and Chavanne, loc. cit.)

Oxide.	Density.	[a] _D .	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. experimental.
Methylamyl Ethylamyl Propylamyl N-Butylamyl Isobutylamyl Cetylamyl Benzylamyl	0.802 (22°)	+0.61	218 882 574 878 878 104 807	134 ·2 150 ·3 166 ·4 182 ·5 182 ·5 375 ·7 192 ·8	135-3 (18°) 152-8 (18°) 166-0 (18°) 180-4 (22°) 186-3 (22°) 887-6 (22°) 195-4 (22°)

This series, it will be seen, has a maximum product of asymmetry in the case of the propylamyl term, whilst the maximum rotation was found for the next higher one, namely, normal butylamyl oxide. The series presents certain features which do not occur in any of the others to which I have previously referred, for whilst the methyl and ethyl terms exhibit no evidence of association, such evidence is exhibited in a slight degree by the propyl, and in a higher degree by the normal butyl, term, or, in other words, precisely for that term where the maximum rotation occurs. The suspicion is naturally aroused that this maximum rotation is connected with the abnormal molecular volume of the term in question. It will be noticed, also, that the isobutyl compound, which bears no evidence of association, has a much lower rotation than the normal butyl compound. The fact of the maximum rotation, however, remains, for the rotation even of the isobutyl compound is greater than that of any of the other terms, excepting the benzyl, which, in consequence of its very different structure, may be excluded from consideration for the present. There is, however, another circumstance which must be taken into account before accepting this series as a verification of the predictions furnished by the product of asymmetry. From Guye and Chavanne's paper, it appears that the methyl, ethyl, propyl, and cetyl compounds were all prepared by the action of sodium amylate on the

iodides of the respective radicles, whilst the normal and isobutyl compounds were obtained by the action of amylic bromide on sodium butylate and isobutylate respectively. Thus, in the preparation of all those oxides which yielded the lowest rotations, sodium was made to act on amylic alcohol, a procedure which is well known to be the most effective method of rendering this alcohol inactive, whilst in the preparation of the two butyl compounds, which gave the highest rotations, the amylic alcohol was not submitted to the direct action of sodium. There can be no doubt that this circumstance renders it necessary to receive the rotation results obtained with reserve.

In the following tables, the values for the several known series of ethereal salts derivable from tartaric acid are investigated; the data are those given by Freundler (Thesis, Paris, 1894).

	Density.	[a] _D .	Product of asymmetry. P × 106.	Mol. vol. calculated for 15°.	Mol. vol. experimental.
	Eth	ereal salts of	tartaric acid	l.	
Methylic Ethylic Propylic Isopropylic Butylic	1·3284 (20°) 1·2059 (20°) 1·1844 (20°) 1·1800 (20°) 1·098 (19°)	+2.14 (20°) +7.66 (20°) +12.44 (20°) +14.88 (20°) +10.3 (19°)	- 354 - 318 - 280 - 280 - 245	139·1 171·3 203·5 235·7	184 0 (20°) 170 8 (20°) 206 8 (20°) 207 1 (20°) 238 6 (19°
	Ethereal salts of dipropionyltartaric acid.				
Methylic Ethylic Propylic Butylic Isobutylic	1·181 (15°) 1·124 (14°) 1·098 (15°) 1·068 (15·5°) 1·073 (16·5°)	-10·7° (15°) +0·4 (16°) +5·6 (16°) +6·9 (12°) +11·4 (19°)	+118 0 -92 -163	244.5 276.7 308.9 841.1	245°5 (15°) 282°9 (14°) 315°1 (15°) 350°2 (15°5°) 848°5 (16°5°)
	Ethereal salts of dibutyryltartaric acid.				
Methylic Ethylic Propylic Butylic Isobutylic	1·145 (14°) 1·105 (15·5°) 1·067 (15·5°) 1·048 (16°) 1·050 (16°)	-15·1° (13°) -0·8 (16°) +5·2 (13°) +6·0 (14°) +8·5 (19°)	+194 +92 0 -78	276·7 308·9 841·1 373·3	277·7 (14°) \$18·1 (15·5°) \$50·5 (15·5°) \$88·6 (16°) \$82·8 (16°)
Ethereal salts of divaleryltartaric acid.					
Ethylic Propylic Butylic	1·101 (18°) 1·068 (12°) 1·050 (16·5°) 1·081 (18°) 1·082 (18·5°)	-16·1° (15°) -2·0 (15°) +3·3 (17°) +4·8 (15°) +7·4 (18°)	+248 +163 +78 0	808·9 841·1 878·8 405·5	814·2 (18°) 850·2 (12°) 882·8 (16·5°) 417·1 (18°) 416·7 (18·5°)
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	Density.	[a] _₽ -	Product of asymmetry. P × 10 ⁶ .	Mol. vol. calculated for 15°.	Mol. vol. experimental.
	Etherea	l salts of dica	proyltartar i c	acid.	
Methylica Ethylic Propylic Isobutylic	1.027 (15°)	-15.9° (16°) -3.1 (16°) +2.2 (16°) +6.0 (16°)	+282 +215 +141 +7	841·1 878·8 405·5 437·7	346·9 (14°) 388·2 (14·5°) 418·7 (15°) 452·1 (13°)
	Ethereal	salts of di-iso	valeryltartar	ic acid.	
Methylic Ethylic Propylic Isobutylic	1.067 (17.5°) 1.049 (18.5°)	-18.9° (14.5°) -1.4 (16.0°) +0.7 (16.0°) +5.7 (16.0°)	+248 +163 +78 0	808 9 841 1 878 8 405 5	312·5 (16·5°) 850·5 (17·5°) 883·6 (18·5°) 418·3 (18·0°)
	Ethereal s	alts of di-isob	utyryltartari	c acid.	
Methylic Ethylic Propylic Isobutylic	1·095 (17·0°) 1·066 (16·0°) 1·048 (16·5°)	-13·4°* (17·0°) -1·5 (17·5°) +2·2 (18·0°) +8·4 (14·0°)	+194 +92 0 -78	276·7 308·9 341·1 273·3	816·0 (17·0°) 850·8 (16·0°) 883·6 (16·5°)
	* The methylic compound being solid, its rotation was only determined in alcoholic solution.				
	Density.	[a] _D .	Product of asymmetry.	Mol. vol. calculated for 15°.	Mol. vol. experimental.
Ethereal sal	Ethereal salts of di-monochloracetyltartaric acid. (P. Frankland and Patterson, Trans., 1898, 73, 193.)				
Methylic 1 · 4 Ethylic 1 · 8 Propylic Butylic	250 (14°) 806 (15·5°) —)·80° (14°) ·40 (15·5°)	+ 221 + 128 + 38 - 2	282·5 264·7 —	232·8 (14°) 269·8 (15·5°) —
Ethereal salts of di-dichloracetyltartaric acid. (P. Frankland and Patterson, loc. cit., 190.)					
Methylic 1 'Ethylic 1 'Propylic Butylic	5108 (15°) 4187 (16°) —	1.97° (19.2°) 6.80 (16°)	+801 +251 +187 +120	252·7 284·9 —	264·7 (15°) 302·7 (16°)
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_	Density.	[a] _b ,	Product of asymmetry.	Mol. vol. calculated for 15°. Mol. vol. experimental	i.
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(P. Frankland and Ethereal salts of mono-trichloracetyltartaric acid. Patterson, loc cit., 186.)

	1·3926 (15°) —	+8·29° (17°) +15·30 (12°) —	-206-380 = -586 -124-420 = -544 -67-440 = -507 -32-441 = -478	240.1	214·5 (17°) 252·4 (15°) —
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In the case of the neutral tartrates and diacidyltartrates, the groups attached to each of the two asymmetric carbon atoms being identical, the product of asymmetry given in the above tables refers to one carbon atom only, whilst in the monacidyltartrates, the groups attached to the two asymmetric carbon atoms being different, each of these carbon atoms has a product of asymmetry of its own. Thus, this is the case with the ethereal salts of monotrichloracetyltartaric acid above.

The above table shows that, in the simple tartrates, there is evidence of association in the case of the methylic compound, and in all the other series of derivatives the molecular volume of the methylic compound, although in excess of that calculated by Traube's formula, is markedly less in excess than are the molecular volumes of the higher homolgues.

In the case of methylic tartate, again, there is some independent evidence that association leads to a movement of the rotatory power in the negative direction, for it has been shown by Freundler (loc. cit.) that methylic tartrate is very highly associated in benzene solution (a molecular weight of 411 instead of the theoretical 178 having been obtained) and that in benzene solution, also, the specific rotation is -5.1° instead of +2.14°, the value found for the pure substance in the fused state. This inference is based, of course, on the assumption that methylic tartrate is more associated in benzene solution than in the fused state, an assumption which is justifiable if Traube's formula be capable of revealing the degree of association.

That a substance may be more associated in solution than in the liquid state appears not to be without precedent, thus the molecular weight of phenol as determined by the Ramsay and Shields method is given by Ramsay and Aston (Trans., 1894, 65, 168) as

Temperature.	Mol. wt.	•
46 — 78°	133.5)	
78 —131· 7	126.9	$C_0H_5 \cdot OH = 94$
131.7—184.0	110.9)	Digitized by Google

whilst the following values were obtained by Beckmann (Zeit. physikal. Chem., 1888, 2, 727—730) with the cryoscopic method in benzene solution (melting point of benzene = 5.44).

Phenol in benzene solution, per cent.	Depression of freezing point.	Mol. wt.
0.337	0·115°	144
1.199	0.385	153
2.481	0.755	161
3.970	1.155	168
7.980	2.080	188
17:29	3.795	223
26.77	5 ·205	252

On reviewing the figures given in the above tables, it is impossible not to be impressed with the fact that it is only in the case of those series in which the product of asymmetry attains a maximum at or about the propylic or butylic terms that there is any even approximate coincidence between this maximum and the maximum rotation in the series, and the suspicion naturally arises as to whether this maximum rotation is not really dependent on the associated nature of the first few terms of the series leading to abnormal rotations of these initial terms, and not to the existence of a maximum product of asymmetry at all.

This suspicion is increased by the circumstance that in series, like that of the tartrates, in which the product of asymmetry continuously diminishes from the first term, there is, notwithstanding, a maximum rotation at or about the same region (that is, the propylic) of the series. Again, in the series of the diacetylglycerates in which the product of asymmetry does not attain a maximum until the thirteenth term, the maximum rotation is already exhibited by the fourth or butylic term.

It would appear, therefore, that the coincidence between theory and experiment, in the matter of maximum product of asymmetry and maximum rotation, may be quite accidental, and the idea that Guye's suggestive speculation receives any support from this occasional coincidence must at present be received with much reserve.

If the conception of the product of asymmetry be laid aside, it would be anticipated that, in ascending an homologous series, the rotation should either continuously increase or decrease, the increments and decrements respectively becoming less and less marked with growing molecular weight. On examining the several series referred to in the tables above, it will be seen that this is actually the case in the following.

1.—Acetylmalates (diminishing rotations, excepting a slight rise in the case of the propylic term, series known up to isobutylic)

- 2.—Propionylmalates (diminishing rotations, but only the methylic and ethylic terms known).
- 3.—Butyrylmalates (diminishing rotations, excepting a slight rise in the case of the propylic term, series known up to isobutylic).
- 4.—Isobutyrylmalates (diminishing rotations, but only the methylic and ethylic terms known).
- 5.—Isovalerylmalates (diminishing rotations, series known up to isobutylic term).
- 6.—Bromacetylmalates (diminishing rotations, excepting a slight rise in the case of the ethylic term, series known up to isobutylic).
- 7.—Chlorosuccinates (diminishing rotations, series known up to diamylic term).
- 8.—Methoxysuccinates (diminishing rotations, series known up to normal butylic term).
- 9.—Ethoxysuccinates (diminishing rotations, series known up to normal butylic term).
- 10.—Benzoylmalates (diminishing rotations, but only the methylic and ethylic terms known).
- 11.—Orthotoluylmalates (diminishing rotations, but only methylic and ethylic terms known).
- 12.—Metatoluylmalates (diminishing rotations, but only methylic and ethylic terms known).
- 13.—Paratoluylmalates (diminishing rotations, but only methylic and ethylic terms known).
- 14.—Dibenzoylglycerates (diminishing rotations, known up to amylic term).
- 15.—Acetyllactates (diminishing rotations, but only methylic and ethylic terms known).
- 16.—Chloropropionates (diminishing rotations, series known up to propylic terms).
- 17.—Bromopropionates (diminishing rotations, series known up to propylic term).
- 18.—Valerates, excluding valeric acid itself (diminishing rotations, series known up to isobutylic term).
- 19.—Dimonochloracetylglycerates (increasing rotations, but only methylic and ethylic terms known).
- 20.—Di-dichloracetylglycerates (increasing rotations, but only methylic and ethylic terms known.
- 21.—Di-trichloracetylglycerates (increasing rotations, but only methylic and ethylic terms known).
- 22.—Di-dichloracetyltartrates (increasing rotations, but only methylic and ethylic terms known).
- 23.—Mono-trichloracetyltartrates (increasing rotations, but only methylic and ethylic terms known).

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- 24.—Dibenzoyltartrates (diminishing rotations, series known up to butylic term).
- 25.—Di-orthotoluyltartrates (diminishing rotations, only methylic and ethylic terms known).
- 26.—Di-metatoluyltartrates (diminishing rotations, only methylic and ethylic terms known).
- 27.—Di-paratoluyltartrates (diminishing rotations, only methylic and ethylic terms known).

In ascending some series, although the influence on rotation is continuously in the same direction, the process is attended with a change of sign.

- 1.—Dipropionyltartrates (series known up to butylic term, change of sign at ethylic term).
- 2.—Dibutyryltartrates (series known up to butylic term, change of sign at propylic term).
- 3.—Divaleryltartrates (series known up to butylic term, change of sign at propylic term).
- 4.—Dicaproyltartrates (series known up to butylic term, change of sign at propylic term).
- 5.—Di-isovaleryltartrates (series known up to butylic term, change of sign at propylic term).
- 6.—Di-isobutyryltartrates (series known up to butylic term, change of sign at propylic term).
- 7.—Di-monochloracetyltartrates (only methylic and ethylic terms known, change of sign at ethylic term).

In ascending other series, again, a maximum rotation is attained which is followed by decline.

- 1.—Malates. The maximum is reasonably explicable as due to the association of the initial terms.
- 2.—Lactates. The maximum is reasonably explicable as due to the association of the initial terms.
- 3.—Tartrates. The maximum, although coincident with association of the early terms, is too pronounced to be thus accounted for.
- 4.—Glycerates. The maximum, although coincident with association of the early terms, is too pronounced to be thus accounted for.
- 5.—Diacetylglycerates. The maximum, although coincident with association of the early terms, is too pronounced to be thus accounted for.
- 6.—Amylic oxides. Rotation results doubtful in consequence of variable mode of preparation.

The grounds for asserting above that the maximum rotation exhibited by the malates and lactates respectively is "reasonably explicable as due to the association of the initial terms" are (1) that strong evidence of such association is furnished by the molecular

volumes, and (2) that in the substitution compounds (acetylmalates. alkoxysuccinates, acetyllactates, chloropropionates, &c.) in which there is little or no evidence of association, the rotation of the methylic is greater than that of the ethylic compound, whilst the rotations of methylic malate and lactate are inferior to those of ethylic malate and lactate respectively. In fact, in the case of the malates. some substitutions raise the lavorotation whilst others depress it. but in both cases the resulting rotations point to methylic malate having a greater layorotation than ethylic malate. The latter statement is at first sight negatived by the fact that the chlorosuccinates, alkoxysuccinates, chloropropionates, and bromopropionates have a dextrorotation diminishing from the methylic term upwards, which would appear to mean that these substitutions had shifted the rotation in the positive direction by a certain amount in each case. and that, starting with the lower rotation of methylic malate and lactate respectively, this had, therefore, resulted in a higher dextrorotation for methylic chlorosuccinate, chloropropionate, and bromopropionate than for the corresponding ethylic compounds. We know, however, that in the transformation of the malates into the chlorosuccinates, and of the lactates into the chloro- and bromo-propionates. an inversion takes place, and that the chlorosuccinates, chloro- and bromo-propionates really corresponding with the original malates and lactates from which they are derived are more highly levorotatory than those malates and lactates themselves. In the case of the alkoxysuccinates, it is not known with certainty to which of the optically isomeric malates they are directly related, but I venture to suggest from their analogy to the chlorosuccinates that the dextrorotatory alkoxysuccinates correspond with the dextromalates, and the recent investigations of Purdie and Lander (Trans., 1898, 78, 287) in which alkoxysuccinates of high laworotation were obtained by acting with alkyl iodides on ordinary (levo-) silver malate leave little room for doubt that this is actually the case.

On the other hand, I have stated above that the maximum rotation exhibited in the series of tartrates, glycerates, and diacetylglycerates cannot satisfactorily be referred to the occurrence of association in the case of the earlier terms of these series, because (1) the maximum is so very pronounced, and (2) because in the numerous substitution compounds which are known, and which exhibit little or no evidence of association, the relationship between the rotation of the methylic and ethylic compounds is retained. Thus methylic glycerate has a lower lavorotation than ethylic glycerate. When the lavorotation is increased, as by the introduction of two acetyl, chloracetyl, or dichloracetyl groups, the methylic compound remains throughout of inferior

lævorotation to that of the ethylic compound. Again, when the lævorotation is depressed (or rather exchanged for a strong dextrorotation), as by the introduction of two benzoyl groups, the methylic compound retains its lower lævorotation, that is, has a higher dextrorotation than the ethylic compound.

Similarly, methylic tartrate has a lower dextrorotation than ethylic tartrate; and when the dextrorotation is increased, as by the introduction of two dichloracetyl groups, or one trichloracetyl group, the dextrorotation of the methylic compound remains inferior to that of the ethylic compound, whilst when the dextrorotation is depressed (or even exchanged for lævorotation), as in the majority of the diacidyltartrates, the dextrorotation of the methylic compound remains inferior to that of the ethylic, or, in other words, in these cases the methylic compound has a higher lævorotation than the ethylic.

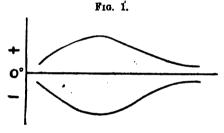
But whilst this occurrence of a maximum cannot thus be explained away in the case of the glycerates, diacetylglycerates, and tartrates. it can also not be justifiably used as a confirmation of the predictions of the product of asymmetry, for in the series of tartrates the product of asymmetry diminishes in ascending from the methylic term, in the diacetylglycerates the maximum product of asymmetry is not reached until the thirteenth term, whilst in the glycerates alone is there approximate coincidence between maximum product of asymmetry and maximum rotation. Is it not equally, or more, possible that the maximum rotation in these series is dependent on the number of atoms attached in a chain to the asymmetric carbon atom? According to the commonly accepted views of stereochemistry, a continuous chain of five carbon atoms will all but return upon itself, and, beyond this further additions to the chain will lead to such interference as must necessitate a readjustment of the exact positions occupied by the carbon atoms in a shorter chain. It is surely highly probable that this stereochemical change should be betrayed by some irregularity in the rotatory manifestations, for example, by the exhibition of a maximum rotation in those series in which the ascent of the series leads to an increase in the rotatory power.

It is obvious, too, that in those series the ascent of which is attended with continuous diminution in the rotation, some irregularity—a minimum rotation—is to be anticipated on stereochemical grounds when the growing chain attached to the asymmetric carbon atom attains the magnitude of five atoms or thereabouts. So far, however, the number of known terms in the several series of this kind is insufficient to detect this irregularity or minimum rotation. The series of the ethereal salts of amylic alcohol, as pointed out on

p. 358, and that of the diacetyltartrates * may be regarded as exhibiting a minimum rotation, for growth of the one group leads to diminution of the original rotation of the first member of the series, but this diminution leads at once to the zero line being crossed, and with successive additions to the group there is increasing rotation of opposite sign (equivalent to diminishing rotation of the original sign) until a maximum rotation of the opposite sign (equivalent to minimum rotation of the original sign) is attained, on which follows diminishing rotation of the opposite sign (equivalent to increasing rotation of the original sign).

The rotation phenomena exhibited in the ascent of homologous series would appear to be capable of classification into the following three types.

a.—Increase in rotatory power up to a maximum, followed by a decline becoming more or less asymptotic, as indicated by the curves in Fig. 1.



To this type belong the glycerates, diacetylglycerates, and tartrates; these series are actually known beyond the occurrence of the maxi-

* The data concerning the rotation of the diacetyltartrates are somewhat imperfect, and they have, in consequence, not been included in the preceding tables. The following figures are given by Freundler (loc. cit.).

Methylic diacetyltartrate in solution in absolute alcohol $t=25^{\circ}$, l=2, $c=2^{\circ}4813$, $a_{p}=-46'$, $[a]_{p}=-15^{\circ}1^{\circ}$.

Ethylic diacetyltartrate in superfused state $t=25^{\circ}$, l=1, $\alpha_{p}=+5^{\circ}$, whilst in solution in absolute alcohol $t=25^{\circ}$, l=2, c=7.088, $\alpha_{p}=+3^{\circ}$, $[\alpha]_{p}=+0.4^{\circ}$.

Propylic diacetyltartrate in superfused state $a_D = +13.4$, l=1, whilst in solution in absolute alcohol $t=23^{\circ}$, l=2, c=4.9872, $a_D=+57'$, $[a]_D=+9.6^{\circ}$.

Butylic diacetyltar trate in liquid state $t=16^{\circ}$, l=1, d=1.096, $\alpha_{D}=+8.8^{\circ}$, $[\alpha]_{D}=+8.0^{\circ}$, whilst in solution in absolute alcohol $t=22^{\circ}$, l=2, c-6.9425, $\alpha_{D}=+1^{\circ}$ 12', $[\alpha]_{D}=+8.8^{\circ}$.

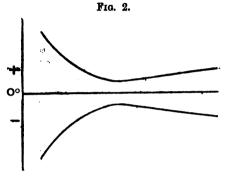
Isopropylic diacetyltarirats in solution in absolute alcohol $t=20^{\circ}$, l=2, c=5.5885, $a_{D}=+41'$, $[a]_{D}=+5.9^{\circ}$.

Isobutylic diacetyltartrate in liquid state $t=18.5^{\circ}$, l=2, d=1.096, $a_{D}=+37^{\circ}$ 8', $[a]_{D}=+17.0^{\circ}$, in solution in absolute alcohol $t=16^{\circ}$, l=2, c=5.4659, $a_{D}=+1^{\circ}$ 18', $[a]_{D}=+11.8^{\circ}$.

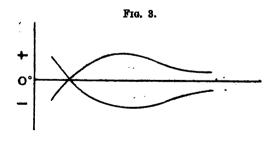
These figures show incontestably that, for the normal series of radicles, the maximum dextrorotation is possessed by the propylic term.

mum. It is to be anticipated that, when sufficiently explored, the dimonochloracetylglycerates, di-dichloracetylglycerates, di-trichloracetylglycerates, di-dichloracetyltartrates, and monotrichloracetyltartrates will each exhibit a maximum in the vicinity of the butylic term.

b.—Diminution in rotatory power down to a minimum, followed by a rise with diminishing increments, as indicated by the curves in Fig. 2.



To this type belong the chlorosuccinates, ethoxysuccinates, methoxysuccinates, chloropropionates, bromopropionates, acetyllactates, acidylmalates, benzoylglycerates, and valerates. Thus in ascending these series, as far as they are known, the rotations continuously diminish, but it is to be anticipated that they will respectively exhibit a minimum when they are more fully explored.



c.—Diminution in rotatory power, accompanied sooner or later by change of sign, the series exhibiting a maximum with a sign the reverse of that of the initial member of the series, as indicated by the curves in Fig. 3.

To this type belong the diacetyltartrates, which series begins with a strong lævorotation for the methylic term, the ethylic term being already dextrorotatory, and this dextrorotation attains a maximum for the propylic term, normal butylic diacetyltartrate being already of distinctly inferior dextrorotation.

Change of sign is similarly exhibited by the dipropionyltartrates dibutyryltartrates, dicaproyltartrates, di-isobutyryltartrates, and di-isovaleryltartrates, also by the dimonochloracetyltartrates, but in none of these has the maximum dextrorotation yet been displayed.

I would add, in conclusion, that it appears not improbable that the many exceptional physical and chemical properties manifested by the initial terms of homologous series of carbon compounds, including the greater tendency of these initial terms to associate, are attributable to stereochemical causes.

I am indebted to the Government Grant Research Fund for the means for carrying out the investigations referred to in this paper.

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XXXV.—Detection and Determination of Sucrose in the Presence of Lactose.

By EDWIN DOWZARD.

SEVERAL methods have been proposed for the detection and determination of sucrose in lactose, but, so far as the author is aware, these have either been a combination of optical and chemical methods, or simply chemical methods.

The following method, with which good results have been obtained, is purely polarimetric, and depends on the fact that sucrose is inverted by citric acid, whereas lactose remains unaltered.

Ten grams of the sample under examination are dissolved in about 70 c.c. of water, the solution boiled for 2 minutes (this is necessary, as lactose exhibits the phenomenon of birotation), and after cooling, made up to 100 c.c., and filtered if necessary; the optical rotation is then determined at 16° in a 200 mm. tube, using an instrument of the Laurent half-shadow type, the reading being taken from the sugar scale (100 sugar divisions = $+21^{\circ}40'$).

Fifty c.c. of the above solution, equivalent to 5 grams of lactose, are now boiled for 10 minutes with 1 gram of citric acid, and, after cooling, the liquid is made up to 100 c.c.; the rotation is then determined as before at 16°. If the sample is pure, the rotation will be half that of the original solution; if sucrose is present, the result will be less than half, owing to inversion.

 $20^{\circ}623$ grams of lactose ($C_{12}H_{22}O_{11}+H_2O$) dissolved in 100 c.c. of water, and examined in a 200 mm. tube, will give a reading of +100 sugar divisions.

A solution of 16.29 grams of sucrose in 100 c.c. of water, before inversion, causes a deviation of 100 divisions to the right, whilst after inversion it has a levorotatory power equal to 34.6 divisions at 16°; consequently, it has undergone an optical change equivalent to a rotation of 134.6 divisions.

Therefore, every 0.1 gram of sucrose present in 10 grams of lactose will, after inversion, cause a decrease in the rotation of 0.8256 divisions.

The figures given below are those obtained in the examination of two samples of lactose, of which the first is pure, the second containing 5 per cent. of sucrose.

Pure lactose.

Sugar divisions.
+48.5
$+24.3 \times 2 = +48.6$
+48.5
+48.6

Lactose containing 5 per cent. sucrose.

	SIGNL CIAMIOUN
Ten grams in 100 c.c	+48.8
Fifty c.c. of above solution after boiling	
with 1 gram of citric acid and making	
up to 100 c.c	$+22.3 \times 2 = +44.6$
Before inversion	+48.8
After inversion	+ 44.6
48.8 - 44.6 = 4.2/0.8256 =	5.08.
Sucrose present	
found	_

The above figures point to the usefulness of this method, as, by its means an admixture of 1 per cent. of sucrose with lactose can be detected with certainty.

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XXXVI.—Note on Certain Isomeric Tertiary Benzylthioureas.

By Augustus Edward Dixon, M.D.

The existence of isomerism amongst tertiary thioureas in which all three radicles are different, appears, so far, to have been established only in the ethylphenylbenzyl class. It is singular that the melting points of the three isomerides are nearly identical, notwithstanding the differences as regards grouping of the contained radicles, and distribution of the masses within the molecule. n-Benzyl-v-ethylphenylthiourea, CH₂Ph·N:C(SH)·NPhEt, and n-ethyl-v-phenylbenzylthiourea, NEt:C(SH)·NPh·CH₂Ph, both melt at 91°, agreeing, moreover, so closely in appearance and general properties that, without very careful examination, one might easily pass for the other; they are distinguishable, however, by the action of ammonia, which at 100° decomposes the former into benzylthiourea and ethylaniline; the latter, at 125°, into ethylthiourea and benzylaniline. The third, NPh:C(SH)NEt·OH₂Ph, melts at 95° (Trans., 1891, 59, 564; 1892, 61, 540).

Of the corresponding methylic derivatives, two only have been prepared, namely, n-methyl-r-phenylbenzylthiourea, NMe:C(SH)·NPh·CH₂Ph, and n-benzyl-r-methylphenylthiourea, CH₂Ph·N:C(SH)·NPhMe. It was remarked in a paper published some years ago (Trans., 1893, 63, 540) that, amongst known phenylated isomeric tertiary thioureas, the member containing the group PhN: had a higher melting point than either of the others; an opportunity has now been taken of ascertaining whether this is also the case as regards the third isomeride, NPh:C(SH)·NMe·CH₂Ph; some further isomeric forms have also been obtained, of which a short account is given.

n-Phonyl-v-methylbenzylthiourea, NPh:C(SH)·NMe·CH₂Ph.—Prepared by mixing alcoholic solutions of phenylthiocarbimide and methylbenzylamine; heat was evolved, and, on cooling, white crystals separated, the yield being quantitative. When purified by recrystallisation from boiling alcohol, very brilliant, long, silvery prisms were obtained melting at 129—130° (corr.).

0.2256 gave 0.2068 BaSO₄. S = 12.61. $C_{15}H_{16}N_{2}S$ requires S = 12.51 per cent.

The substance is nearly insoluble in boiling water, moderately soluble in boiling, but only sparingly in cold, alcohol, very freely in chloroform, moderately freely in hot benzene and carbon bisulphide, rather sparingly

in ether. Its alcoholic solution is not darkened by boiling with alkaline lead tartrate, but is desulphurised by heating with neutral nitrate of silver; the ammoniacal nitrate gives a white, curdy precipitate, which dissolves on boiling. The melting temperature lies distinctly above those of its isomerides; n-methyl-r-phenylbenzylthiourea melts at 121°, whilst the n-benzyl-r-methylphenyl compound melts at 85°.

Desulphurisation.—Effected by boiling the alcoholic solution with the calculated quantity of silver nitrate, filtering, and adding water cautiously to the filtrate; the scaly, yellowish precipitate produced, after treatment with animal charcoal and recrystallisation from spirit, was obtained in broad, thin, pearly needles, melting, not quite sharply, at 134—135° (corr.).

Found (by wet combustion) C = 74.72. $C_{15}H_{16}N_{2}O$ requires C = 74.96 per cent.

The urea is insoluble in water, freely soluble in hot alcohol, moderately in cold.

n-Benzyl-v-methylbenzylthiourea, CH₂Ph·N:C(SH)·NMe·CH₂Ph.—Prepared, as before, from benzylthiocarbimide and methylbenzylamine; the product left on evaporating the spirit was a transparent oil, showing no tendency to become solid even after being kept for several days over sulphuric acid in a vacuum. When steam distilled, and set aside in a desiccator, crystals began to appear at the end of a month, and eventually the whole mass solidified. By treatment with animal charcoal and several recrystallisations from weak alcohol, the compound was obtained in shining, vitreous needles melting at 73° (uncorr.).

0.2039 gave 0.1765 BaSO₄. S = 11.90. $C_{16}H_{18}N_{2}S$ requires S = 11.86 per cent.

It is practically insoluble in water or light petroleum, sparingly soluble in hot caustic potash (this solution is not affected by boiling with a lead salt), freely in benzene or alcohol; the latter solution is desulphurised by warming with ammoniacal nitrate of silver.

n-Methyl-v-dibenzylthioures, NMe₂:C(SH)·N(CH₂Ph)₂.—Prepared from methylthiocarbimide and dibensylamine, the yield being practically quantitative. The product occurred in brilliant, white, apparently rhombic crystals, insoluble in water and light petroleum, easily soluble in alcohol, ether, chloroform, benzene, and carbon bisulphide; it also dissolves in cold sulphuric acid, from which it is precipitated, on the addition of water, as a curdy solid.

Found, S = 12.31. $C_{16}H_{18}N_{9}S$ requires S = 11.86 per cent.

With alkaline lead, or ammoniacal silver, solution, it behaves like the isomeride described above; from this it is easily distinguished,

however, not only by its crystalline form and appearance, but also by the great difference in fusibility; it melts at 110—111° (corr.).

A third isomeride of the two preceding compounds is known, namely, methyl-wnv-dibenzylthiourea, CH₂Ph·N:CMe·NH·CH₂Ph, obtained by Reimarus (*Ber.*, 1886, 19, 2348) from ab-dibenzylthiocarbamide and methylic iodide; it is a basic oil.

n-Methyl-v-methylbenzylthiourea, NMe:C(SH)·NMe·CH₂Ph.—From methylthiocarbimide and methylbenzylamine; when recrystallised from weak spirit, it formed vitreous, flattened crystals insoluble in water, easily soluble in alcohol, and melting sharply, without decomposition, between 87.5° and 88.5° (uncorr.).

Found, S = 16.23. $C_{10}H_{14}N_{2}S$ requires S = 16.51 per cent.

The alcoholic solution is not affected by boiling with alkaline lead tartrate; ammoniacal nitrate of silver yields no precipitate, but the mixture slowly darkens in the cold, or blackens at once on heating, with formation of a brilliant speculum.

n-Benzyl-v-dimethylthiourea, CH₂Ph·N:C(SH)·NMe₂.—Prepared from alcoholic benzylthiocarbimide and 33 per cent. aqueous dimethylamine; it formed an oil, which slowly solidified. When recrystallised from spirit, in which it is very freely soluble at the boiling point, but only moderately in the cold, it was obtained in well-formed, vitreous prisms, insoluble in water and melting at 98·5—99·5° (corr.), that is, 11° above its isomeride just described. Carbon was estimated by wet combustion with chromic acid.

Found, C = 61.72. $C_{10}H_{14}N_{2}S$ requires C = 61.79 per cent.

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XXXVII.—On Lössner's Benzoylethyloxysulphocarbamic Acid; and the Formation of Pseudoureas.

By Augustus Edward Dixon, M.D.

It is now about seventeen years since Will (Ber., 1881, 14, 1489) showed that the alkylogens combine directly with symmetrical disubstituted thiocarbamides to form the haloid salts of basic substances which are isomeric with the corresponding trisubstituted thioureas.

All thioureas and thiocarbamides, excepting such as are already completely substituted, appear to be capable of undergoing this change, which results in the transference of the alkylic radicle, not to the nitrogen, but to the sulphur of the thio-compound, with formation

of an imidothiocarbamate; for example, $CS(NHPh)_2 + EtI = NPh:C(SEt)\cdot NHPh + HI$. For such isomeric forms, the generic name "pseudothioureas" has been proposed (Trans., 1895, 67, 565).

Amongst the ureas, a change of this kind is not known to occur; moreover, the pseudothioureas, when desulphurised by metallic salts, fail to afford the corresponding pseudo-ureas, decomposing instead, with formation of a mercaptide. The class, in short, appears to be hitherto unknown, with the exception of a single representative, obtained not long ago by Stieglitz, which will be referred to later on. In the present communication, I propose to show that Lössner's so-called "unsymmetrical ethylbenzoylurea" is not NH₂·CO·NEt·COPh, but COPh·N:C(OEt)·NH₂, and that the train of operations whereby it was produced constitutes a general synthetical method for obtaining acidic disubstituted members of the pseudo-urea class.

Lössner found (*J. pr. Chem.*, 1874, [ii], 10, 237) that on adding benzoic chloride to a hot, saturated alcoholic solution of potassium thiocyanate, potassium chloride separates, and the mixture, when cooled and carefully treated with water, deposits a compound, $C_{10}H_{11}NSO_{2}$, in yellow prisms, melting, when pure, at 73—74°. The action is explained as occurring in two stages,

$$KONS + C_6H_5 \cdot COCl = KCl + C_6H_5 \cdot CO \cdot CNS$$
;

the latter product does not appear as such, but unites at once with the alcohol, yielding the new compound, benzoylethylsulphocarbamic acid.

$$C_6H_5 \cdot CO \cdot CNS + C_2H_5 \cdot OH = C_{10}H_{11}NSO_2.$$

Ethylic benzoate is simultaneously formed, owing to interaction between the alcohol and the acid chloride.

With cold alcoholic potash, the substance affords a potassium derivative, $C_{10}H_{10}NSO_2K$; on boiling with alcohol, the latter is decomposed, mainly as follows, $C_{10}H_{10}NSO_2K + 2KHO = C_6H_5 \cdot COOK + KCNS + C_2H_5 \cdot OH + H_2O$, but partly, also, with evolution of ammonia,

$$C_{10}H_{10}NSO_2K + 5KHO = C_8H_5 \cdot COOK + K_2CO_8 + K_2S + NH_8 + C_9H_5 \cdot OH + H_9O;$$

ethylamine was looked for in the escaping gases, but proved to be absent.

By boiling with silver, lead, and other salts, metallic sulphides are formed, and when heated alone, hydrogen sulphide, mercaptan, &c.; from all these properties, Lössner concludes (p. 244) that the structure of this compound should be represented by the formula

$$CO \left\{ \begin{array}{l} N \left\{ \begin{array}{l} CO \cdot C_6H_5 \\ C_2H_5 \end{array} \right., \text{ or, possibly (p. 259), } CS \left\{ \begin{array}{l} N \left\{ \begin{array}{l} CO \cdot C_6H_5 \\ C_2H_5 \end{array} \right. \end{array} \right. \right. \right.$$

the ethylic group is attached to nitrogen, and not through an oxygen atom, he infers on the ground that a substance like $CS < NH \cdot CO \cdot C_6H_5$ would have no acid properties, since it is an 'ether.'

The potassium salt, then, is regarded as CO NEt. COPh; with ethylic bromide, it yields an oil, decomposed by ammonia into mercaptan, and an "unsymmetrical ethylbenzoylurea," presumably isomeric with the substance obtained later on by Miquel (Ann. Chim. Phys., 1877, [v], 11, 318) by desulphurising ab-ethylbenzoylthicarbamide, COPh.NH. CS.NHEt, with yellow oxide of mercury. Miquel's compound is said to melt at 192°; the melting point of Lössner's is not given; they both are said to crystallise from alcohol in rhombohedra.

How the compound C₁₀H₁₁N₂SO is supposed to be produced does not seem altogether clear; the formula of the ethylic bromide derivative is stated to be COPh·NEt·CO·SEt;* the potassium compound would, therefore, be COPh·NEt·CO·SK; Lössner, however, remarks (p. 260) that it must be assumed that, on formation of either of these compounds out of the "acid," the sulphur and oxygen exchange But if so, the acid itself should be COPh·NEt·CS·OH, and not COPh·NEt·CO·SH, as represented. Moreover, if benzoyl thiocyanate be taken as the intermediate product, it is difficult to understand how it could unite with the alcohol to produce either form. In effect, although he nowhere actually states it, Lössner seems to go on the assumption that benzoylthiocarbimide is really produced, inasmuch, at least, as he represents, in the final stage, the benzoyl group as directly attached to the nitrogen. Three years later, all uncertainty was removed by Miquel, who showed (loc. cit.) that benzoylthiocarbimide and ethylic alcohol unite spontaneously to form Lössner's "benzoylethyloxysulphocarbamic acid."

But, according to Lössner's view, the ethyl group is also attached to nitrogen. If this were the case, either form of compound must, on hydrolysis, yield ethylbenzamide, or else ethylamine; yet on boiling with potash and passing the gaseous products into hydrochloric acid, ammonia alone was found, the ethylic group being eliminated as alcohol; with the derivatives, similar results were observed, the ethylic residue coming off as alcohol or mercaptan, but never as amine.

Singularly enough, it was Lössner himself who established the absence of organic bases in the above decompositions, and it therefore seems curious that he should have proposed such formulæ. Miquel, in an important footnote, calls attention to this discrepancy, and criticises severely the grounds on which its discoverer infers the

^{*} Because with potash it yields alcohol, mercaptan, ammonia, and alkali carbonate.

"acidity" of the compound $C_{10}H_{11}NSO_2$:—1, because it is neutral; 2, because aqueous alkalis decompose it without forming compounds [salts]; 3, because it can give no salts, either with amines, or with metallic oxides, or carbonates. According to Miquel, it is an 'ether,' $CS < NH \cdot C_7 H_5 O^{\bullet}$, and its potassium compound is ethylic potassiobenzoylsulphocarbamate, $CS < NK \cdot C_7 H_5 O$.

The constitution here represented has an advantage over Lössner's, in accounting for the non-formation of ethylamine on hydrolysis; nevertheless, it is by no means free, itself, from difficulty. For if the potassium compound is similarly constituted to the ethyl compound (as Miquel affirms), there seems to be no particular reason why the ethylic bromide derivative, obtained from the latter, should not equally be CS $<_{\text{O} \cdot \text{C}_3}^{\text{N}(\text{C}_2\text{H}_5) \cdot \text{C}_7\text{H}_5\text{O}}$; but, if so, it is surprising that cold ammonia should instantly decompose it, whilst the production, in this interaction, or even without the presence of ammonia at all, of mercaptan is scarcely intelligible. Moreover, the ethylic bromide derivative gives, with caustic alkali, mercaptan and ammonia (together with benzoic acid and carbonic anhydride), † for which reason the group SEt must be regarded as forming an integral part of the molecule. whilst the second ethylic group is obviously not attached to nitrogen. There appears to be only one structure consistent with all these $COPh\cdot N: C < S \cdot C_0 \cdot H_5$, that is, the substance is namely, reactions. diethylic imidobenzoylthiocarbonate.

Now the potassium salt which gives this substance must be either (a) COPh·N:C $\stackrel{\text{SK}}{\smile}$ or else, as stated by Miquel, (b)

COPh·NK·CS·OEt;

but, on account of the well-known 'deforming' effect of alkylogens on thiocarbamidic, and, perhaps, thiocarbamic, compounds, it cannot safely be asserted that form b is incapable of yielding, with ethylic bromide, the above imidothiocarbonate; and hence it is not possible, on the data, to certainly assign either constitution to the potassium derivative. That a mere exchange of C_2H_5 for K occurs is the simplest view, and, in the absence of any contrary evidence, it is here provisionally adopted. Then, unless the caustic alkali itself

COPh'N:C(\tilde{S} Et)*OEt + 2H₂O = COPh'NH₃ + EtSH + EtOH + CO₂. The melting point of benzamide is 128°, that of ethylbenzamide, 67°.

^{*} Beilstein (Handb.) gives the formula, 'NH(C7H5O) CO SC2H5 (1)."

[†] By heating this compound with water at 105°, Lössner obtained mercaptan, together with a substance melting at 128—129°, which he did not identify, but reserved for later study; doubtless it was benzamide produced thus

deforms the original molecule (which there is no reason to suppose), the series of changes may be represented as follows: $COPh \cdot N : CS + EtOH = COPh \cdot N : C < COPh \cdot N : COP$

This additive product yields the derivative, COPh·N:C SK, which, in turn, affords, with ethylic bromide, the compound COPh·N:C SEt, a substance whose formula does not seem to admit of any reasonable doubt.

As stated above, Lössner gives no melting point for the compound produced by acting with ammonia on the latter thiocarbonate; it was therefore prepared, in order to verify its isomerism with Miquel's ab-benzoylethylurea. With a view to avoid the secondary action which occurs in Lössner's method of operating, the benzoic chloride was not allowed to come in contact with the alcohol until it had previously been converted into the corresponding thiocarbimide.

Benzoylthiocarbimide was first isolated by Miquel (loc. cit.), according to whose directions it is prepared by allowing benzoic chloride (free from phosphorus oxychloride) to stand for several days in contact with dry lead thiocyanate, heating then in an oil-bath at 160°, exhausting the mixture with dry ether, and fractionating the extract in a vacuum. I find that it can be much more conveniently obtained, in solution, by boiling the chloride, in dry benzene, with excess of the lead salt and filtering. The yield, if care be taken, is almost quantitative, and the whole process can easily be completed, for a 20-gram batch, inside fifteen minutes. A charge, prepared in this way, was mixed with excess of absolute alcohol, and the mixture gently warmed on the water-bath, and set aside; after evaporation of the solvents, an oil was left which, when it had become solid, was powdered, pressed between bibulous paper to remove a trace of ethylic benzoate, and weighed; the yield amounted to over 88 per cent. of the theoretical, calculated from the weight of benzoic chloride employed. After one recrystallisation from 80 per cent. alcohol, it was obtained in sulphur-yellow needles melting at 72-73°, and possessing all the properties of Lössner's compound (m. p. 73-74°), save that its alcoholic solution, instead of being neutral, was faintly acid to litmus. Miquel points out that Lössner's method gives a poor yield, on account of loss, from direct interaction between the alcohol and benzoic chloride. The above modification of Miquel's process is preferable as being quicker and much less laborious.

The potassium salt prepared from the 'thiourethane' according to Lössner's directions (yield about 70 per cent. of the theoretical) was converted into the ethyl derivative by digestion with absolute alcohol

and ethylic iodide; after separation of the potassium iodide, the cold alcoholic solution was saturated with dry gaseous ammonia, whereby mercaptan was expelled, and the solution, on concentration, deposited rhombohedral crystals—in short, Lössner's results were corroborated in every particular. When purified by recrystallisation from weak spirit, the compound was pure white, odourless, and free from sulphur; it melted at 74—75° (corr.) without decomposition, and hence was not identical with ab-benzoylethylures. To make certain that it really was the isomeride, a portion was burnt for nitrogen.

0.2032 gave 26.4 c.c. moist nitrogen at 15° and 742 mm. N=14.83. $C_{12}H_{12}N_2O_2$ requires N=14.62 per cent.

If this compound were, as supposed by Lössner, aa-benzoylethylurea, COPh·NEt·CO·NH₂, the lowness of its melting point would be remarkable, considering that the symmetrical isomeride melts at 192° according to Miquel.* But it is not the aa-compound; it is decomposed on hydrolysis, as Lössner himself found, into carbonic and benzoic acids, alcohol, and ammonia, a change which he seeks to explain as follows.

$$NH_2 \cdot CO \cdot N(C_2H_5)C_7H_5 \cdot O + 3KHO + H_2O = C_6H_5 \cdot COOK + K_2CO_8 + 2NH_3 + C_2H_5 \cdot OH.$$

It is evident that these phenomena do not satisfactorily accord with the constitution assigned, as such a compound should give ethylamine, and its absence shows that the ethylic group is not engaged with a nitrogen atom. Moreover, the parent substance could not, at least directly, afford the urea in question.

$$COPh \cdot N : C < \frac{SEt}{OEt} + NH_8 = EtSH + COPh \cdot N : C < \frac{NH_2}{OEt}.$$

The product melting at 74° is thus not a true urea, but a substance isomeric with the benzoylethylureas; it bears towards the carbamides proper a relation similar to that subsisting between the pseudothioureas on the one hand, and the corresponding true thiocarbamides on the other.

$$\begin{array}{lll} \text{CS} & \stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}{\stackrel{\text{NH}_2}}}}}}}}}}}}$$

By analogy with their sulphuretted congeners, these compounds may conveniently be named pseudoureas; according to the system of nomenclature which I have elsewhere proposed for thio-derivatives, the

^{*} This melting point is too high; see post.

substance in question would be known as ethyl- ψ n-benzoylurea. The mono- and di-substituted ψ -thioureas have usually low melting points as compared with their isomerides in which the sulphur is not engaged with an organic radicle; the relative ease with which the above urea melts is, therefore, a point of resemblance between oxy- and thiocompounds of this class.

Hitherto, no ψ -ureas containing acid radicles have been recognised, but the type itself is not unknown, a single representative of it containing one alkyl and two benzenoid radicles having been obtained a few years ago (Stieglitz, *Ber.*, 1895, 28, 573) by the action of sodium ethoxide on carbodiphenylimide in alcoholic solution at -5°

$$C(NPh)_2 + EtOH = PhN: C < \frac{NHPh}{OEt}$$

It is described as an oil; the isomeric ethylcarbanilide, NPhEt·CO·NHPh,

(from phenylic isocyanate and ethylaniline), is a solid melting at 91°. Methyl-ψn-benzoylurea, C₆H₅·CO·N:C(OCH₈)·NH₂.—Methylic imidobenzoylthicarbonate, which was prepared in the same way as its ethylic homologue, the yield in this case being practically quantitative, had the properties attributed to it by Miquel. An attempt to obtain its sodium derivative by treating the ethereal solution with sodium ethoxide gave an unsatisfactory result, but the alcoholic solution, when mixed with alcoholic potash, afforded the corresponding potassium compound, COPh·N:C(OMe)·SK. When washed with ether, it formed yellowish crystals, somewhat like iodoform in appearance; it is freely soluble in water, moderately in alcohol or acetone, and melts at about 208°, evolving mercaptan. Yield, about 80 per cent. of the theoretical.

The potassium compound, dissolved in nearly anhydrous alcohol, was boiled with ethylic iodide, and the solution, poured off when cool from the precipitate of alkali iodide, was saturated with gaseous ammonia. Mercaptan was evolved, and the liquid, on concentration, solidified to a crystalline mass, which was extracted with boiling acetone; the solution presently deposited a white solid, still containing traces of potassium iodide, which was removed by cold water, and the dried residue recrystallised from light petroleum. Thus purified, the substance occurred in beautiful, fern-like masses of white, flattened crystals, having a brilliant, pearly lustre, and melting, without decomposition, at 77—78°.

The formula was checked by a nitrogen determination.

0.2114 gave 29 c.c. moist nitrogen at 15.5° and 760 mm. N = 16.02. $C_9H_{10}N_2O_2$ requires N = 15.77 per cent.

The compound is slightly soluble in boiling water, from which it is deposited, on cooling, in oily droplets which soon crystallise; it is very freely soluble in alcohol, ether, and chloroform, easily in benzene and warm carbon bisulphide, rather sparingly in boiling, and very sparingly in cold, light petroleum. Its dilute alcoholic solution is not changed by ammoniacal silver nitrate.

In order to ascertain whether the methyl and benzoyl groups were attached to a single nitrogen atom, the substance was heated with 10 times its weight of water, in a sealed tube, first at 105°, and then at 125°, but without any sign of change. On raising the temperature to 150—160°, action occurred, and carbonic anhydride escaped on opening the tube, the liquid contents of which smelt of ammonia and methylic benzoate; the white, erystalline solid which was present proved to be a mixture of benzoic acid with a little benzamide. The production of methylic benzoate is significant as showing the presence of a methoxyl group, but the temperature of decomposition was too high for the benzamide to escape hydrolysis. Another experiment was therefore made, by boiling the substance with a large excess of caustic potash, passing the alkaline vapour into hydrochloric acid, and evaporating this solution to dryness; the white, solid residue had the appearance and properties of ammonium chloride, and as it showed no sign of deliquescence after exposure in an open dish for a day and a night to ordinary (damp) air, it was, presumably, free from methylamine hydrochloride. That this was the case was established by dissolving the salt in water, precipitating the solution with chloroplatinic acid, and determining the amount of metal in the platinochloride.

0.255, after ignition, left 0.1122 Pt. Pt = 43.83. (NH₄)₀PtCl₆ requires Pt = 43.91 per cent.

Consequently, the alkaline gas is ammonia alone.

In another similar experiment, the gases were passed into water, acidified with hydrochloric acid, and a fraction distilled off from the solution, using a Glynsky's tube. This gave the reduction test when warmed with potassium dichromate and dilute sulphuric acid, thus pointing to the presence of methylic alcohol. From the alkaline residue of hydrolysis, pearly crystals of potassium benzoate were deposited on cooling.

These results may be summed up by the equation,

$$\begin{aligned} \mathbf{C_6H_5 \cdot CO \cdot N \cdot C(OCH_8) \cdot NH_2 + 3H_2O &= \mathbf{C_6H_5 \cdot COOH} + \mathbf{CO_2} + \\ & 2\mathbf{NH_8 + CH_8 \cdot OH.} \end{aligned}$$

If the compound were $C_6H_5 \cdot CO \cdot N(CH_8) \cdot CO \cdot NH_2$, methylamine, together with ammonia, would be formed on hydrolysis, whilst, on the other hand, methylic alcohol (or methylic benzoate) would be absent.

For the purpose of comparison, symmetrical benzoylmethylurea, isomeric with the above ψ -compound, was prepared by desulphurising the corresponding thiocarbamide.

ab-Benzoylmethylthiocarbamide, C₆H₅·CO·NH·CS·NH·CH₈, obtained from benzoylthiocarbamide and methylamine, and purified by recrystallisation from alcohol, formed colourless, thick prisms, melting at 151—152° (corr.).

0.2056 gave 0.245 BaSO₄. S=16.38.

 $C_9H_{10}N_2SO$ requires S = 16.51 per cent.

It is very sparingly soluble in boiling water, moderately in boiling alcohol, and easily in warm, dilute caustic alkali; the latter solution is desulphurised by heating with alkaline lead tartrate.

ab-Benzoylmethylurea, $C_6H_5\cdot CO\cdot NH\cdot CH_3$.—This was prepared by adding the calculated quantity of silver nitrate, in dilute alcohol, to a boiling alcoholic solution of the preceding compound; the filtrate from the silver sulphide, on cooling, deposited the urea in tufts of shining needles melting, after recrystallisation, at $170-171^\circ$ (corr.).

0.206 gave 28 c.c. moist nitrogen at 20° and 768 mm. N = 15.82. $C_0H_{10}N_2O_2$ requires N = 15.77 per cent.

It is slightly soluble in boiling water, not very freely in hot alcohol, and sparingly in cold.

There is a considerable discrepancy between the melting points recorded by Miquel and by Leuckart (J. pr. Chem., 1880, [ii], 21, 33) for ab-benzoylethylurea. The former, as already stated, gives 192°* (but no analysis is appended); the latter, who obtained it from ethylurea and benzoic chloride, gives 168°. The preparation was undertaken, with the following results.

ab-Benzoylethylthiocarbamids was prepared, as usual, from benzoylthiocarbimide and ethylamine, and on concentration, splendid large, thick prisms were deposited. These were twice recrystallised from alcohol, the first recrystallisation raising the melting point by 1°, whilst the second did not alter it, the substance (vitreous needles) now melting finally at 130—131° (corr.); Miquel gives 134°. It is soluble in warm, dilute, caustic potash, and the solution is desulphurised by boiling with lead tartrate.

By treatment with silver nitrate, the urea was obtained in long needles which were several times recrystallised from spirit; they were quite colourless, free from silver, and melted at 114—114.5° (corr.).

^{*} This is also its molecular weight.

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0.205 gave 0.4738 CO<sub>2</sub> and 0.1233 H<sub>2</sub>O. C = 63.02; H = 6.68. 0.2014 ,, 0.4621 CO<sub>2</sub> ,, 0.1206 H<sub>2</sub>O. C = 62.57; H = 6.65. 0.204 ,, 26.4 c.c. moist nitrogen at 17.5° and 763 mm. N = 15.02. C_{10}H_{12}N_2O_2 requires C = 62.46; H = 6.26; N = 14.62 per cent.
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The whole preparation was repeated, with the same result; the product crystallised from boiling water, in which it is somewhat sparingly soluble, in beautiful, long, hair-like, flexible needles melting at the same temperature as before.

That the use of silver nitrate, instead of mercuric oxide, as a desulphurising agent, could affect the properties of the urea produced, seemed unlikely; but to make certain, the compound was once more prepared using mercuric oxide; the product melted at 114—115°, and differed in no respect from that obtained by the use of the silver salt.

The following experiments, made with a view to obtain disubstituted and higher ureas, in which an acid and non-acid radicle are engaged with a single nitrogen atom, may not be devoid of interest.

In one, ethylthiccarbimide was caused to act on sodium acetanilide* in presence of alcohol, in the hope of realising the change.

the latter would easily afford NPhAc · CS · NHEt, whence, by desulphurisation, the urea could be obtained. The metallic anilide, however, seemed to play a similar part to caustic alkali, yielding a thiourethane (together with acetanilide),

$$EtNCS + EtOH = EtNH \cdot CS \cdot OEt [or EtN:C(SH) \cdot OEt].$$

Similar results were obtained with phenylthiocarbimide.

In another, sodium acetanilide and methylphenylcarbamic chloride, NPhMe COCl, were employed, both in absolute alcoholic solution; sodium chloride was deposited, but the only other definite compound which could be isolated from the residual liquor was acetanilide.

In a third, sodium acetanilide and phosgene were tried, in the hope of possibly obtaining a chloride, NPhAc COCl, which, with ammonia, might afford NPhAc CO NH₂. The phosgene, however, was completely dechlorinated, but the product, strange to say, was not diacetyl-carbanilide, as might have been expected, but acetylcarbanilide.

* It does not unite at ordinary temperatures with acetanilide alone. But it combines easily with sodium cyanamide, although not with cyanamide (Wunderlich, Ber., 1886, 19, 449), and hence it seemed worth while to try the sodium compound of acetanilide.

Anisoylthiocarbimide and its Derivatives.

Experiments on the same lines as those with benzoylthiourethane, using the corresponding anisoyl compound, led to similar results; the anisoylthiocarbimide, $CH_3O \cdot C_6H_4 \cdot CO \cdot NCS$, required was prepared as usual by heating the acid chloride, dissolved in benzene, with lead thiocyanate; the clear, pale yellowish-brown, practically odourless solution thus obtained was easily desulphurised by lead and silver salts. Advantage was taken of the opportunity to prepare a number of other derivatives, an account of which is given below.

Ethylic imidoanisoylthiocarbonate (anisoylthiourethane), $CH_{\bullet}O \cdot C_{\bullet}H_{\bullet} \cdot CO \cdot N \cdot C(SH) \cdot OC_{\bullet}H_{s}$.

—Obtained by gently warming the thiocarbimide in benzene with excess of absolute alcohol; the velvety mass of yellow crystals left on evaporating the solvents, crystallised from light petroleum in rosettes of snow-white, microscopic needles melting at 70—71°. The yield was 94 per cent. of that theoretically obtainable from the weight of anisoyl chloride employed.

0.2059 gave 0.2 BaSO₄. S = 13.35. $C_{11}H_{18}NO_{3}S$ requires S = 13.41 per cent.

The substance is slightly soluble in boiling water, and is deposited, on cooling, in oily droplets which soon crystallise; it dissolves easily in alcohol, benzene, chloroform, carbon bisulphide, and aqueous potash; the last named solution is moderately easily desulphurised by boiling with alkaline lead tartrate. Ammoniacal nitrate of silver gives a curdy, white precipitate, soluble on heating; the solution gradually darkens when boiled.

The potassium compound was obtained by mixing alcoholic potash (1 mol.) with the concentrated alcoholic solution of the thiourethane (1 mol.), and washing the solid product with ether; it formed white crystals, freely soluble in water, moderately in alcohol, sparingly in ether, and melting, with effervescence, at about 222° (uncorr.).

It was dissolved in spirit, boiled with ethylic iodide, and saturated with ammonia, in the same way as the corresponding benzoyl compound, and with like results; the solid product, after being broken up, washed with water, and recrystallised first from chloroform and then from light petroleum, formed vitreous, pointed prisms, softening slightly at 67° and melting at 69—70°.

0.207 gave 22.9 c.c. moist nitrogen at 17° and 763 mm. N = 12.96 $CH_2O \cdot C_6H_4 \cdot CO \cdot N \cdot C(NH_2) \cdot OC_2H_5$ requires N = 12.64 per cent.

Ethyl-un-anisoylurea is very sparingly soluble in boiling water,

sparingly in hot light petroleum, but freely in alcohol, chloroform, benzene, and hot carbon bisulphide.

Working on the above lines, several attempts were made to obtain a phenylic analogue, NPh:C(OEt)·NH, but without success.

Anisoylthiourea, $CSN_2H_3 \cdot CO \cdot C_6H_4 \cdot OCH_8$.—Separated at once, on mixing alcoholic ammonia with the benzene solution of the thiocarbinide; yield, 83 per cent. of the theoretical. It was deposited from spirit in mixed rhombs and octahedra, vitreous and brilliant, melting at $216-217^{\circ}$ (corr.).

0.2014 gave 0.2263 BaSO₄ S = 15.45. $C_0H_{10}N_2O_0S$ requires S = 15.25 per cent.

The substance is practically insoluble in boiling water, rather sparingly soluble in boiling alcohol, very sparingly in cold, freely in chloroform and hot benzene, and moderately in warm carbon bisulphide; the benzene solution is precipitated on adding light petroleum. It is also soluble in warm, dilute, caustic potash; this solution is readily desulphurised by heating with lead tartrate, and gives, with hydrochloric acid, a precipitate which does not dissolve in excess of acid.

Anisoylthiohydantoin (n-Anisoylthiourantoin) (Trans., 1897,71,638).—Anisoylthiourea was fused with monochloracetic acid; the product, after being well washed with spirit, formed a pale-yellow powder, insoluble in water or the usual organic solvents, but easily soluble in dilute potash to a clear, bright red solution, which is precipitated by hydrochloric acid, the precipitate being soluble in excess of the acid. Heated in a narrow tube, it sinters and darkens at about 222°, and is blackened and decomposed at 230° (uncorr.). The solution in alkali is very slightly desulphurised by boiling with lead tartrate, owing, probably, to the presence of a trace of unchanged thiourea; when boiled alone, the solution gives the iron reaction for thioglycollic acid. It is almost insoluble in alcohol; the solution gives, with ammoniacal silver nitrate, a yellowish, amorphous precipitate, which scarcely darkens on boiling. The product thus appears to be, substantially at

least, anisoylthiourantoin, $CH_3O \cdot C_6H_4 \cdot CO \cdot N : C < \frac{S - CH_2}{NH \cdot CO}$.

0.204 gave 0.1952 BaSO₄. S = 13.15. $C_{11}H_{10}N_3SO_8$ requires S = 12.81 per cent.

ab-Anisoylphenylthiocarbamide, CH₃O·C₆·H₄·CO·NH·CS·NHC₆H₅.

—Heat was evolved on mixing the constituents, and yellowish crystals presently separated, the yield amounting to 90 per cent. of the theoretical. By recrystallisation from spirit, brilliant, vitreous prisms were obtained, melting at 125·5—126° (corr.).

0.2014 gave 0.1677 BaSO₄. S = 11.45. $C_{15}H_{14}N_{2}O_{2}S$ requires S = 11.20 per cent.

The substance is insoluble in water, easily soluble in boiling alcohol, rather sparingly in cold, moderately in carbon bisulphide, freely in acetone, benzene, and chloroform: the last two solutions are precipitated on adding light petroleum. It is easily desulphurised by heating with lead tartrate, and, with ammoniacal silver nitrate, yields a white precipitate which is blackened on warming. The solid dissolves in warm dilute caustic alkali, separating out again unchanged when the solution cools.

ab-Anisoylorthotolylthiocarbamids.—Over 92 per cent. of the theoretical yield was obtained; the product, when recrystallised from alcohol, formed almost colourless prisms, melting at 126.5° (corr.).

Found, S = 10.89. $C_{16}H_{16}N_9SO_2$ requires S = 10.68 per cent.

It is insoluble in water, easily soluble in hot alcohol, rather sparingly in cold, and is desulphurised by silver and lead salts, like the phenylic homologue.

ab-Anisoylparatolylthiocarbamids.—This compound separated at once when the paratoluidine was added; the yield amounted to 95 per cent. of the theoretical. When recrystallised from alcohol, it formed colourless prisms, melting at 127—128° (corr.).

Found, S=10.9; Calculated, 10.68 per cent.

Its properties resemble those of the ortho-derivative.

ab-Anisoylmethylthiocarbamids.—Prepared from 33 per cent. aqueous methylamine; the yield was only 58 per cent. of the theoretical. The recrystallised substance occurred in colourless prisms, melting at 143—144° (corr.), and gave 14.42 per cent. of 8, against 14.30 required. It is slightly soluble in water, otherwise its properties resemble those of the preceding compound.

ab-Anisoylethylthiocarbamids.—Prepared like the methylic homologue; the yield in this case was nearly quantitative. After recrystallisation, it formed thick prisms, melting, without decomposition, at $126.5-127.5^{\circ}$ (corr.). A sulphur determination gave 13.68 per cent., against 13.46 required for $C_{11}H_{14}N_2SO_2$. Its properties are similar to those of the methyl compound, except that it is rather more soluble in alcohol. It dissolves in warm, dilute alkali; with hydrochloric acid, this solution gives a white precipitate, soluble in excess of the acid.

ab-Anisoylethylurea.—Obtained by desulphurising the preceding compound with silver nitrate; it formed lozenge-shaped, vitreous crystals, softening slightly at 145° and melting at 146—147° (corr.), that is, 77° above the ψ -isomeride.

0.2009 gave 0.4402 CO₂ and 0.121 H_2O . C=59.75; H=6.69. 0.2074 ,, 23.4 c.c. moist nitrogen at 19° and 768 mm. N=13.10. $C_{11}H_{14}N_2O_3$ requires C=59.42; H=6.32; N=12.65 per cent.

It is sparingly soluble in boiling water or cold alcohol, moderately in boiling alcohol, easily in warm, dilute caustic potash.

ab-Anisoylbenzylthiocarbamide.—From the thiocarbimide and benzylamine; yield, 91 per cent. of the theoretical. When recrystallised from alcohol, in which it is moderately soluble at the boiling point but very sparingly in the cold, it formed colourless prisms, melting at 127—128° (corr.).

Found, S = 10.91. $C_{16}H_{16}N_2SO_2$ requires S = 10.68 per cent.

Its properties are similar to those of the ethylic compound. n-Anisoyl-v-phenylbenzylthiourea,

CH₈O·C₆H₄·CO·N:C(SH)·N(C₆H₅)·CH₉C₆H₅.

—From benzylaniline; the yield was nearly quantitative. After three recrystallisations (from alcohol), the compound, when seen in mass, still retained a faint yellow colour; it occurred in brilliant, rhombic plates, sintering at 141° and melting at 142—143° (corr.).

Found, S = 8.81. $C_{22}H_{20}N_2O_2S$ requires S = 8.52 per cent.

It is insoluble in water, only moderately soluble in boiling alcohol, sparingly in cold, or in light petroleum, easily in benzene. The alcoholic solution is not desulphurised by boiling with alkaline lead tartrate; ammoniacal nitrate of silver in excess gives a white precipitate which darkens only very faintly on heating. The presence of sulphur is easily recognised, however, by the evolution of hydrogen sulphide when the solid is heated in a dry tube.

 \bar{I} desire to express my thanks to Mr. \bar{R} . E. Doran, for help afforded in the course of this work.

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XXXVIII.—Action of Metallic Thiocyanates on Certain Substituted Carbamic and Oxamic Chlorides; and a New Method for the Production of Thiobiurets.

BY AUGUSTUS E. DIXON, M.D.

Concerning the action of lead and other metallic thiocyanates on halogenised organic compounds, a number of communications have recently been made from this laboratory. (Trans., 1895, 67, 565,

1040; 1896, 69, 855, 1593; 1897, 71, 617); the present paper includes an account of results obtained with the chlorides of certain nitrogenous acids.

So far as data are yet available, the nature of the interaction between inorganic thiocyanates and halogenised organic compounds appears to depend mainly on the way in which the halogen is attached, although its occurrence and extent are further influenced by the presence or absence of solvent, the nature of the solvent, the temperature, the particular inorganic radicle employed, and the time occupied in withdrawing the halogen.

As regards the first point, every compound hitherto examined containing the group –CO·Cl united with an organic radicle, under suitable conditions exchanges its halogen for the thiocyanic residue, the product in each case functioning towards primary and secondary amines, alcohols, phenylhydrazine, and lead or silver solutions, not as a true thiocyanate, but as a thiocarbimide. Dicarboxylic acid chlorides yield analogous derivatives, for instance, C₂H₄(CO·NCS)₂, and carbonyl chloride itself, if heated with lead thiocyanate in presence of toluene, affords much thiocarbimidic product, whether CO(NCS)₂ or not is still uncertain.

From ordinary thiocarbimides, these acidic compounds differ in being more or less easily decomposable by water, with formation of thiocyanic acid or carbonyl sulphide; moreover, some of them, although uniting readily with amines, are broken up on contact with ammonia into a corresponding amide and thiocyanic acid; it may be that the unstable forms are tautomeric.

The chlorine united with certain negative groups other than carbonyl is similarly exchangeable; thus thionyl chloride, sulphuryl chloride, chlorosulphonic acid, ethylsulphuric and phenylsulphonic chlorides all interact with metallic thiocyanates, affording thiocarbimidic products; but so far as they have yet been examined, these actions run less smoothly, and the complete withdrawal of the halogen appears to be a matter of difficulty. Phosphorus trichloride easily yields a substance having the general properties of an unstable acidic isothiocyanate, which is desulphurised by lead and silver salts, and combines spontaneously with aniline, to form a solid decomposable by water, with production of phenylthioures. The study of this interesting action is still incomplete, but it seems as though the first product were phosphorus isothiocyanate, P(NCS)₈, and the second, phosphorus triphenyltrithiourea, P(NH·CS·NHPh)_s, the latter undergoing hydrolysis into phenylthiourea and an acid of phosphorus. Similar results have been obtained using phosphorus oxychloride.

It is well known that halogen in non-acidic combination can also be exchanged, but the products have no longer a thiocarbimidic

character; thus with ethylic bromide, benzylic chloride, ethylic monochloracetate, and so on, the process may be carried out in alcoholic solution, since true thiocyanates are formed, whilst if an acid chloride be employed under like conditions, the end-product (unless the chloride be itself destroyed by the alcohol) is a substituted thiourethane. It may be noted that substitution of NCS for the halogen in such 'negative' attachment is much more rapidly effected than when SCN replaces it in a purely hydrocarbon radicle; thus it is possible, from chloracetyl chloride, CH₂Cl·COCl, to directly obtain the derivative CH₂Cl·CO·NCS (Trans., 1897, 71, 620).

It is not clear, from the above results, whether the introduction of

-NCS or -SCN groups in place of a halogen is in some way dependent on whether or not the original compound is generally acidic in character. If so, one might expect chloracetylthiocarbimide to pass on, more or less readily, into glycolyldithiocarbimide, CH₂·NCS, but, CO—NCS on the other hand, it is conceivable that the -NCS first introduced might 'protect' the remaining chlorine atom from attack; to test this speculation, some experiments were made with acidic monhalogen compounds. Monochloracetic acid and picryl chloride were employed, under varying conditions as regards temperature, time, solvent, and nature of the metallic thiocyanate; the results may be summarised by stating that the latter gave no detectable thiocarbimide under any circumstances—in fact, it did not appear to interact at all; the former did not altogether escape attack, but the quantity of thiocarbimidic product, even under the most favourable conditions, although sufficient to be easily detected, was but an insignificant fraction of the amount of acid used. Consequently, it would seem that the only halogenised compounds which undergo any material conversion into isothiocyanate, in this way, are those in which the halogen is in direct combination with a negative group.

The object of the present investigation was to ascertain whether the chlorides derived from certain nitrogenised carboxylic acids would undergo change into the corresponding isothiocyanates. Derivatives of carbamic acid were first tried, with a view to obtain a class of substances bearing towards the thiobiurets and ethereal salts of thioallophanic acid a relation somewhat analogous to that subsisting between ordinary thiocarbimides, on the one hand, and the corresponding thiocarbamides and thiocarbamic ethers on the other, and thus to lead up to a general synthetical method for the preparation of such compounds. As yet, the carbamic chlorides derived from benzenoid acids appear to be known only in the form of disubstitution derivatives; * the inter-

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^{*} Unless 'phenylisocyanate hydrochloride' be really NHPh COCl. Whether mono- or non-substituted carbamyl isothiocyanates can exist in the free state remains

action between these alone and metallic thiocyanates is dealt with in the present communication.

Assuming that the various classes of biurets, &c., above referred to are similar in constitution, their relations may be shown by the typical formula.

I. R·NCS. II. RNH·CS·NH₂. III. RNH·CS·OR'.
IV. R₂N·CO·NCS. V. R₂N·CO·NH·CS·NH₂. VI. R₂N·CO·NH·CS·OR

(where R and R' are supposed to be monad hydrocarbon radicles); and, as will be seen in the experimental part, representatives of all three latter classes have now been obtained. The isothiocyanates themselves, IV, could not be isolated, but their existence in solution was established by the production of members of classes V and VI, as well as of certain other derivatives, for instance, thiosemicarbazides, R_xN·CO·NH·CS·NH·NHPh. Not many syntheses have been effected under class VI, benzylic alcohol alone of those employed uniting with the isothiocyanates in question, but the derivatives which have been obtained are interesting as representatives of a class of thioallophanates hitherto unknown.

From phenyloxamic acid, a corresponding isothiocyanate has also been prepared, NHPh·CO·CO·NCS, and from this, in turn, a compound, NHPh·CO·CO·NH·CS·NHPh; in type, it is related to biuret in somewhat the same way as oxamide is to urea.

Amongst substituted thiobiurets, isomerism of position may obviously occur with respect both to radicles and to the sulphur. The typical forms are generally represented as similar to thiocarbamide, NH₂·CS·NH₂, but since the existence is now well established, amongst derivatives of the latter, of substances constituted or acting also on the 'thiourea' type, HS·C(NH)·NH₂, the occurrence of such labile forms amongst thiobiurets might be anticipated; moreover, in the case of certain substituted dithiobiurets, a variety of it has recently been observed (Billeter, Ber., 1893, 26, 1688). From these two causes alone, and without including the forms obtained by Billeter, the number of isomerides possible for a given compound is very high. Thus, a monosubstitution derivative, containing the simplest hydrocarbon radicle, may conceivably exist in ten different varieties three derived from NH₂·CO·NH·CS·NH₂, and seven more from

to be discovered; in such a combination as NHPh CO NCS, the NCS might possibly tend to unite with the NHPh group to form CO $\stackrel{\text{NPh}}{\sim}$ CS (carbonylphenylthio-

carbamide), or else NPh: C NH CS. However, the compound NHPh CO CO NCS appears to be able to exist as such. See p. 409.

NH₂· CO·N:C< NH₂, or NH₂· CO·NH·C< NH₂, whilst if the CONH₂-group be also supposed capable of labile change, the number of isomerides reaches twenty-six. Unfortunately, no adequate nomenclature exists for expressing the constitution of even the known forms in this class of substances.

In this paper, the convention adopted, in order to define the position of substituting groups, is to mark the three nitrogen attachments, a, b, and c respectively, starting from the end atom, next the sulphur.

c. b. a NH₂·CO·NH·CS·NH₂.

For convenience in naming such thioallophanic salts as are represented on the ordinary type, the term thioallophanic acid might be restricted to carboxythiocarbamide, the two nitrogen attachments being indicated, as in other thiocarbamides, by a and b respectively; if oxygen be otherwise replaced by sulphur, the position adjoining b might be marked β , whilst the ψ -symbol would serve, as usual, to indicate mercaptoid forms.

a. b. β . ψ . NH₂·CS·NH·CO·OR.

Derivatives of the typical compounds (1) NH₂·CS·NH·CO·OH, (2) NH₂·CO·NH·CS·OH, and (3) NH₂·CO·NH·CO·SH, would thus be named thicallophanates, β-thicallophanates, and ψ-thicallophanates respectively; the derivatives of dithicallophanic acid might be similarly distinguished. Of the above three typical forms of monothicallophanates, derivatives of (1) and (3) only have yet been recorded, for example, NHPh·CS·NPh·CO·OEt (Seidel, J. pr. Chem., 1885, [ii], 32, 263); NH₂·CO·NH·CO·S·C₂H₅ (Peitzsch and Salomon, ibid., 7, 477); as stated earlier, representatives of (2) are now forthcoming—it may be, however, in a labile form.

Several years ago (Trans., 1893, 63, 318), the author drew attention to a peculiarity of the disubstituted fatty and allylic thiocarbamides namely, that they are not desulphurised by boiling with alkaline solution of lead tartrate, whereas if either (or both) of the groups be benzenoid in character, desulphurisation occurs. Acetyl, benzoyl, and anisoyl groups appear to function, in this respect, similarly to aromatic hydrocarbon radicles, but the group R₂N·CO, contained in

^{*} From its analogy to thiourea, it seems not improbable that monothiobiuret itself should be represented by one of the two latter formulæ; perhaps also the di- and tetra-substituted thiobiurets, described below. But, in the absence of any definite evidence regarding their structure, they are here provisionally represented on the ordinary biuret type.

the thiobiurets described below, seems to play the same part in relation to such desulphurisation as though it were an aliphatic residue; thus, for instance, c-diphenyl-a-methyl (similarly, α -ethyl and α -benzyl) thiobiuret withholds its sulphur, whilst the corresponding c-diphenyl-a- (ortho- and para-)-tolyl compounds give it up.

Alcoholic silver nitrate, as a rule, desulphurises the thiobiurets on warming; this action serves as the basis of a rapid, but not very satisfactory, method for obtaining the corresponding biurets, a few of which, as well as a guanidine-like compound of the biuret class, have thus been prepared.

Some attempts were made to produce biurets through the direct action of carbamic chlorides upon substituted thioureas, for instance, to realise the interaction

 $NPh_2 \cdot CO \cdot Cl + CSN_2H_3Ph = HCl + NPh_2 \cdot CO \cdot N \cdot C(SH) \cdot NHPh.$

Alcoholic solutions were first tried, and subsequently fusion of the mixed constituents, but without success. Thiocarbanilide was employed, with results which are detailed below; benzylethylphenylthiourea gave no better results than the monophenyl compound.

I. Derivatives of Diphenylearbamyl Isothiocyanate.

When lead or copper thiocyanate was heated with diphenylcarbamyl chloride, $(C_6H_5)_gN\cdot COCl$, in presence of alcohol, benzene, or toluene, little or no thiocarbimidic product was obtained, and the addition of zinc dust appeared to exert no influence. Using cumene, a certain amount of action soon took place, although a solution perfectly free from chlorine was not obtained, even after prolonged boiling. With potassium thiocyanate, the phenomena were similar, but on substituting a mercurial salt, the difficulty was overcome. The chloride, dissolved in dry cumene, is mixed with about double the theoretical amount of sifted mercuric thiocyanate, and the mixture (which should contain enough cumene to be freely mobile) rapidly heated, with constant At or near the boiling point, action sets in; the thiocyanate darkens, swells up, and becomes pasty; on cooling, it hardens to a brittle mass, which is ground up in a mortar and the whole filtered and washed; a pale yellow solution is thus obtained, generally free from chlorine—if the latter is still present, it must be removed by boiling up with a fresh charge of thiocyanate and filtering again. The flask should not be too small to allow of vigorous shaking-600 c.c. is a convenient size, preferably of Jena glass, and the conical form is best adapted to the (often troublesome) operation of breaking up and getting out the solid residue. A glass tube serves as condenser and to prevent the vapour from taking fire at the mouth of

the flask; the latter can be comfortably held with a thick asbestos glove. On the whole, it appears best to work with small charges (10 to 15 grams of chloride at a time) in order to get the action completed and the solution cooled without delay.

The liquid thus obtained is devoid of pungent odour, but contains a thiocarbimide in solution; it is desulphurised by boiling with alkaline lead tartrate, and with ammoniacal nitrate of silver yields a precipitate of silver sulphide, even in the cold, but more readily on warming. When brought in contact with nitrogenous bases, action takes place spontaneously, with development of heat and formation of additive compounds; with benzylic alcohol, combination occurs less readily. The formation of the thiocarbimide may be represented by the equation

$$2(C_6H_5)_2N \cdot COCl + Hg(SCN)_2 = 2(C_6H_5)_2N \cdot CO \cdot NCS + HgCl_2;$$

but the yield, under the above conditions, falls considerably short of the theoretical; some desulphurisation occurs, and the solution usually contains traces (and sometimes more than traces) of some yellowish, amorphous, metallic compound.

acc-Triphenylthiobiuret.—On adding aniline (1 mol.), dissolved in benzene, to the cumene solution, the mixture at once became warm, and solid matter presently began to separate. After it had stood for a little, the whitish product was collected and washed, first with benzene and then with light petroleum. When dry, its weight amounted to 62 per cent. of that obtainable according to the equation

$$NPh_2 \cdot CO \cdot NCS + NH_2Ph = NPh_2 \cdot CO \cdot NH \cdot CS \cdot NHPh$$

and reckoned on the quantity of diphenylcarbamic chloride used.

On recrystallisation from boiling acetone, brilliant, pure white needles were obtained, melting at 163—163.5° (corr.); they were dried over sulphuric acid and analysed.

 $0.2 \text{ gave } 0.1386 \text{ BaSO}_4. \quad S = 9.52.$

0.2053 gave 0.1398 BaSO₄. S = 9.36.

0.2134 gave 22.1 c.c. moist nitrogen at 17° and 768 mm. N=12.14. $C_{90}H_{17}N_8SO$ requires S=9.23; N=12.13 per cent.

The compound is therefore, as was expected, a triphenylthiobiuret. It is insoluble in water, very sparingly soluble in ether, sparingly in carbon bisulphide, rather more easily in boiling alcohol and acetone, and moderately so in hot benzene and chloroform. Its alcoholic solution is slowly and imperfectly desulphurised by boiling with alkaline lead tartrate, whilst with silver nitrate a white precipitate is formed, which blackens quickly on the addition of ammonia. Strong nitric acid attacks the substance vigorously on gentle warm-

ing, evolving carbonic anhydride and yielding an orange solution; from this, water precipitates a bright yellow, amorphous solid, apparently a nitro-compound, and the aqueous solution contains sulphuric acid. The above solid is insoluble in cold water, but dissolves easily in warm spirit, forming a lemon-yellow solution, which, on the addition of excess of potash or ammonia, becomes rich scarlet, almost identical in colour with Nencki's beautiful 'rhodanic red.' It was found later that diphenylcarbamic chloride itself behaves similarly.

The compound dissolves in boiling acetic anhydride, with formation of phenylthiocarbimide, which, on adding water, separates in oily droplets, and the residual solution, on cooling, deposits white needles, probably acetyldiphenylcarbamide, NHAc·CO·NPh₂, but the action was not examined in detail.

An attempt was made, by dissolving the substance in (1 mol.) hot potash, and adding silver nitrate, to obtain the corresponding biuret; the product, however, formed brown, sticky granules, which presently changed into a black tar.

a-Orthotolyl-c-diphenylthiobiuret.—On adding the ortho-base, dissolved in benzene, to a freshly prepared solution of the diphenyl compound, the phenomena were similar to those observed in the preceding case, but the yield amounted to only 50 per cent. of the theoretical. By recrystallisation from boiling alcohol, fine, white needles were obtained, melting at 163.5— 164° (corr.). A sulphur determination yielded figures agreeing with those required for the thiobiuret, $(C_6H_5)_2N\cdot CO\cdot NH\cdot CS\cdot NH\cdot C_7H_7$.

0.2102 gave 0.1342 BaSO₄. S = 8.77. $C_{01}H_{10}N_{0}SO$ requires S = 8.87.

The substance is insoluble in water, moderately soluble in boiling alcohol or acetone, rather sparingly in cold. Its alcoholic solution is gradually desulphurised by boiling with alkaline lead tartrate; it is only darkened, in the cold, by ammoniacal nitrate of silver, but blackens at once on heating. Nitric acid vigorously oxidises the solid, yielding sulphuric acid, together with a bright yellow nitrocompound apparently identical with that obtained in like manner from the phenylic homologue.

Desulphwisation.—Alcoholic silver nitrate (2 mols.) was added to the thiobiuret (1 mol.) dissolved in a boiling mixture of chloroform and alcohol, the silver sulphide was removed by filtration, using the pump, and the greenish-brown, clear liquid thus obtained deposited microscopic prisms on cooling. After recrystallisation from spirit, they became slightly moist at 130°, melted at 132—133° (corr.), and gave the following results on analysis.

0.2002 gave 20.9 c.c. nitrogen at 14° and 755 mm. N = 12.19. $(C_6H_5)_2N \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_7H_7$ requires N = 12.20 per cent.

The yield was 63 per cent. of the theoretical.

- a-Diphenyl-c-orthotolylbiuret is insoluble in water, moderately soluble in hot alcohol, sparingly in cold alcohol, ether, and light petroleum, freely in benzene and chloroform. It is scarcely soluble in boiling caustic soda, and, as might be expected, does not give the copper biuret reaction. It is insoluble in hydrochloric, but soluble in sulphuric acid, the solution being precipitated on dilution with water. Nitric acid attacks it vigorously, affording a nitro-compound, in the same way as the parent substance.
- a-Paratolyl-c-diphenylthiobiuret.—Using paratoluidine, a nearly white solid was deposited, which, after being extracted by, and recrystallised from, boiling alcohol, in which it is rather sparingly soluble, was obtained in microscopic needles; it behaves towards solvents in much the same way as the phenylic homologue, and melts at 172—172.5° (corr.).
 - 0.2144 gave 0.1369 BaSO₄. S = 8.77. $(C_6H_5)_2N \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_7H_7$ requires S = 8.87 per cent.

It is desulphurised by alkaline lead salts, or by ammoniacal silver salts, in the same manner as the preceding thio-compounds, and behaves similarly on treatment with nitric acid.

a-Methyl-c-diphenylthiobiuret.—Thirty-three per cent. aqueous methylamine was used, diluted with plenty of absolute alcohol; by recrystallisation from boiling spirit, in which it is only moderately soluble, the product was obtained in soft, white needles, insoluble in water, sintering at 166° and melting at 170—171° (corr.). Alkaline lead solution does not withdraw the sulphur on boiling, but ithe alcoholic solution is immediately blackened, even in the cold, by ammoniacal nitrate of silver.

0.2132 gave 0.174 BaSO₄. S = 11.22. $(C_6H_5)_2N \cdot CO \cdot NH \cdot CS \cdot NH \cdot CH_8$ requires S = 11.24 per cent.

a-Ethyl-c-diphenylthiobiuret.—Prepared, like the preceding, from ethylamine; ice-like plates were deposited which, after a couple of recrystallisations from spirit, formed brilliant, silky, flattened prisms, becoming somewhat electrical on friction, and melting at 137—138° (corr.). The substance is insoluble in water, moderately easily soluble in boiling alcohol, sparingly in cold; it dissolves in warm, dilute, caustic alkali, the solution being precipitated on the addition

^{*} If one hydrogen in each of the two NH-groups in biuret be substituted, the product no longer gives the biuret reaction (H. Schiff, Annalon, 1897, 299, 260).

of excess of hydrochloric acid. With lead and silver salts, it behaves like the methylic homologue.

0.2044 gave 0.1634 BaSO₄. S = 10.99. $C_{16}H_{17}N_{2}SO$ requires S = 10.71 per cent.

a-Benzyl-c-diphenylthiobiuret.—Combination occurred with evolution of heat, the yield of solid product amounting to something over 63 per cent. of the theoretical for the weight of chloride used. After two recrystallisations from alcohol (the second of which did not alter the melting point), the substance was deposited in beautiful tufts of white, feathery needles, sintering a little at 166°, and melting at 167—168° (corr.).

0.2195 gave 0.1412 BaSO₄. S=8.84. $(C_6H_5)_2N\cdot CO\cdot NH\cdot CS\cdot NH\cdot CH_2\cdot C_6H_5$ requires S=8.87 per cent.

The compound is insoluble in water, slowly and sparingly soluble in hot alcohol, very sparingly in cold. With ammoniacal nitrate of silver in the cold, or more readily on warming, its alcoholic solution yields a precipitate of silver sulphide, but it is not desulphurised by boiling with alkaline lead tartrate. Nitric acid acts on this compound in the way previously described; nitrobenzene was also formed.

c-Diphenylthiobiuret.—Alcoholic ammonia, in very slight excess, was added to the solution of the isothiocyanate, and in a few seconds the deposition of solid matter commenced; after recrystallisation, long, thin prisms were obtained, having a faint yellow tinge, and melting at 183° (corr.) to an amber-coloured liquid. Yield, nearly 70 per cent. of the theoretical.

0.2168 gave 0.1904 BaSO₄. S = 12.07. $(C_6H_5)_2N \cdot CO \cdot NH \cdot CS \cdot NH_2$ requires S = 11.82 per cent.

c-Diphenylthiobiuret is insoluble in water, moderately soluble in boiling alcohol, sparingly in cold, easily in dilute caustic alkalis. It is desulphurised, although not readily, by lead tartrate, but gives up its sulphur easily to hot ammoniacal nitrate of silver. With nitric acid, it behaves like its higher substituted allies.

The isomeric ac-diphenylthiobiuret is still unknown; an attempt was made to obtain it by expelling with aniline the ethoxy-group in a-carboxyethyl-b-phenylthiocarbamide (Doran, Trans., 1896, 69, 326), the desired interaction being

 $NHPh \cdot CS \cdot NH \cdot CO \cdot OEt + NH_2Ph =$ $NHPh \cdot CS \cdot NH \cdot CO \cdot NHPh + EtOH.$

Molecular proportions were mixed and carefully heated, whereupon gas was evolved, smelling strongly of mercaptan, and burning with a VOL. LXXV.

bluish flame; the residue presently solidified, and on recrystallisation from alcohol gave a main crop of short prisms, followed by a lesser one consisting of leaflets; when again recrystallised, the latter melted at 130°, and proved to be the unaltered carboxy-derivative. The main product, on the other hand, was practically free from sulphur; it softened at 220°, melted at about 235—236°, and consisted, apparently, of carbanilide.

c-Diphenylthiobiuret and Chloracetic Acid.—Diphenylthiobiuret may obviously be regarded as diphenylcarbamylthiocarbamide (or -thiourea); an experiment was therefore made, in order to learn whether it would behave as a thiourea with chloracetic acid, yielding a thiohydantoin-like derivative.

The former, dissolved in alcohol, was evaporated down on the waterbath with ethylic monochloracetate but this method not proving satisfactory, another portion was carefully fused over an argand burner, with a slight excess of the free acid, until effervescence commenced; the yellow melt was then allowed to solidify, dissolved in warm, dilute alcohol, and the solution exactly neutralised with caustic alkali. On cooling, a solid was deposited which, after recrystallisation from boiling alcohol, was obtained in beautiful tufts of thin, flexible needles, melting at 184—185° (corr.) to a liquid of the colour of bromine. The compound is insoluble in water, moderately soluble in hot alcohol, easily in cold alkali, and when boiled with the latter, gives Andreasch's iron reaction for thioglycollic acid. It is not affected by boiling with alkaline lead solution; with ammoniacal silver nitrate, a white precipitate is soon formed, but it does not blacken, even on boiling.

0.2047 gave 0.1529 BaSO₄. S = 10.26. $C_{16}H_{18}N_{8}SO_{2}$ requires S = 10.30 per cent.

This compound is accordingly the expected n-diphenylcarbamylthiourantoin (nomenclature, Trans., 1897, '71, 638); its formation may be explained (representing the thiobiuret molecule in a labile form) as follows.

$$NPh_{2} \cdot CO \cdot N : C \underbrace{< SH}_{NH_{2}} + \underbrace{CH_{2}Cl}_{CO \cdot OH} = NPh_{2} \cdot CO \cdot N : C \underbrace{< S - CH_{2}}_{NH \cdot CO} + HCl + H_{2}O.$$

a-Benzylphenyl-c-diphenylthiobiuret.—Only a few experiments were made with secondary amines; this is the only case in which any definite compound could be isolated, and the yield was very poor. Benzylaniline was used, the first attempt being a failure; the second time, after concentrating on the water-bath, a clear brown solution was obtained, but it gave no sign of solid matter, even after being kept for many days. It was steam distilled in order to remove solvents, the

residual oil (which now sank in water) mixed with spirit, boiled up with animal charcoal, and heated on the water-bath to drive off the spirit; the treatment with spirit was repeated, and the darkcoloured, thick oil thus obtained, after being kept for some time over sulphuric acid, partially solidified. The solid, when separated from adherent oil, washed, and recrystallised from alcohol, occurred in tufts of white needles, becoming somewhat electrical on friction, and melting at 137-138° (corr.).

0.2099 gave 0.1140 BaSO₄. S = 7.46 $(C_6H_5)_2N \cdot CO \cdot NH \cdot CS \cdot N(C_6H_5) \cdot CH_2 \cdot C_6H_5$ requires S = 7.33 per cent.

This tetra-substituted thiobiuret is insoluble in water, freely soluble in hot alcohol, sparingly in cold, almost insoluble in weak potash. Its alcoholic solution is slowly desulphurised by boiling with alkaline lead tartrate, with formation of a speculum; ammoniacal nitrate of silver blackens it instantly in the cold.

With piperidine, the product was an oil which could not be made to solidify; it contained about 2 per cent. less sulphur than would be required for NPh. CO·NH·CS·N:C,H10.

In the hope of effecting substitution at the remaining nitrogen attachment, benzylethylphenylthiourea and the chloride were heated together in chloroform, in the proportions required for the action

NPh₂·COCl + NHBz·CS·NEtPh = HCl + NPh₂·CO·NBz·CS·NEtPh,

but combination failed to occur under these conditions, and the experiment was not pursued.

a-Diphenylcarbamyl-β-phenylthiosemicarbazide.*—With phenylhydrazine, in benzene, solid matter separated at once; after recrystallisation from boiling spirit, fine, almost pure white needles were obtained, melting at 152.5—153° (corr.).

0.201 gave 0.1294 BaSO₄. S = 8.85. $C_{90}H_{18}N_4SO$ requires S=8.84 per cent.

The interaction may be represented as follows.

 $(C_6H_5)_2N \cdot CO \cdot NCS + C_6H_5 \cdot NH \cdot NH_2 =$ (C₆H₅)₆N·CO·NH·CS·NH·NH·C₆H₅.

The yield was fairly satisfactory, amounting to 76 per cent. of that required by the above equation, and reckoned, as usual, on the amount of chloride taken.

The thiosemicarbazide is insoluble in water, and only sparingly soluble in boiling alcohol; it dissolves in concentrated sulphuric acid, giving a fine, emerald-green solution, which is oxidised by ferric chloride, with formation of a buff-coloured precipitate. Its alcoholic solution, when treated with bleaching powder, acquires a reddish-brown coloration; with Fehling's solution, it becomes deep blue (this colour reaction is very intense), but no reduction occurs, even on boiling. Desulphurisation is not effected by lead or silver salts at the boiling point of the mixtures; but the solid is attacked by strong nitric acid, with formation of sulphuric acid, and of the yellow nitroderivative.

An attempt was made to combine ethylphenylthiosemicarbazide, in hot alcohol, with diphenylcarbamyl chloride, in the hope of obtaining a more completely substituted compound than the above, but without success.

$$NHEt \cdot CS \cdot NH \cdot NHPh + NPh_2 \cdot COCl = HCl + NPh_2 \cdot CO \cdot NEt \cdot CS \cdot NH \cdot NHPh.$$

Benzylic a-Diphenyl-β-thioallophanate.—When excess of benzylic alcohol was mixed with the isothiocyanate, no change appeared to occur in the cold, but on concentrating the mixture on the water-bath, a small quantity of an amorphous, yellowish powder separated, which blackened on heating with caustic alkali, owing to the formation of mercuric sulphide. After a time, the solution deposited thick, yellowish crystals; these were dissolved in boiling spirit, and the solution filtered; the crop of crystals thus obtained consisted of small, vitreous, apparently rhombic, prisms; they softened a little at 140°, and melted at 141—142° (corr.). A sulphur determination gave the figures required for an additive compound.

The compound is insoluble in water, very sparingly soluble in light petroleum, easily in benzene and alcohol; the latter solution is not desulphurised by boiling with alkaline lead tartrate. Ammoniacal nitrate of silver yields a pale, greenish-yellow precipitate, which, on heating, whitens and partially dissolves. Nitric acid vigorously oxidises the solid, producing sulphuric acid, together with the yellow nitro-derivative.

Attempts made to combine other alcohols with diphenylcarbamyl-thiocarbimide did not give satisfactory results. Methylic and ethylic alcohols were boiled with the cumene solution; in another experiment, ethylic alcohol was heated with it at 100°, under pressure, for nearly an hour; in another, cinnamic alcohol was employed, and the mixture steam distilled; but in no case could any definite compound

be isolated. Sodium ethoxide, in absolute alcohol, was tried, but the mixture decomposed, yielding metallic sulphide together with mercaptan.

An attempt to isolate the thiocarbimide by steam distillation met with no better success; thiocyanic acid was found in the aqueous distillate, together with traces of some compound desulphurisable by lead and silver salts; the blackish residue gave up to alcohol a substance containing neither sulphur nor chlorine, it melted at $183-184^{\circ}$ (corr.), and consisted, apparently, of tetraphenylurea, $CO[N(C_6H_5)_2]_2$. The action is doubtless similar to that occurring with many other acidic thiocarbimides, namely,

 $NPh_2 \cdot CO \cdot NCS + H_2O = NPh_2 \cdot COOH + HSCN,$

the former product then decomposing,

 $2\mathbf{NPh_2 \cdot COOH} = \mathbf{CO(NPh_2)_2} + \mathbf{H_2O} + \mathbf{CO_2}.$

II. Derivatives of Methylphenylcarbamyl Isothiocyanate.

In the earlier experiments, methylaniline, dissolved in cumene, was mixed with the theoretical amount of carbonyl chloride in toluene solution, the methylaniline hydrochloride filtered off, and the filtrate then treated, as usual, with mercuric thiocyanate; the yields obtained on treatment with bases were, however, very poor, much oily or tarry product being formed. Subsequently, when the pure carbamic chloride was employed, the solution had little odour; it was pale yellow; if shaken up with cold water and mixed with ferric chloride, a barely perceptible thiocyanic reaction was produced, but if previously boiled with water, a distinct, although not very strongly marked, red coloration appeared. It was desulphurised in the cold by ammoniacal silver nitrate, and by lead salts on heating.

a-Phenyl-c-methylphenylthiobiurst.—In preparing this compound, as in all other cases, except where it is otherwise stated, the base was added dissolved in benzene; on concentrating on the water-bath, some mercuric sulphide was deposited (this happens, to a greater or less extent, in nearly all these preparations), and an oil left which was dissolved in spirit, treated with animal charcoal, and filtered. A sticky product was obtained, which eventually yielded woolly masses of needles, insoluble in water, freely soluble in hot alcohol, moderately in cold, and melting at $158-159^{\circ}$ (corr.). The formula, $CH_3 \cdot (C_6H_5)N \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$, was checked by a sulphur determination.

0.212 gave 0.1777 BaSO₄. S = 11.52. $C_{15}H_{15}N_{3}SO$ requires S = 11.24 per cent.

The alcoholic solution is desulphurised instantly by cold ammoniacal nitrate of silver, and moderately readily by heating with alkaline lead tartrate; the latter property serves to distinguish it from the isomeric a-methyl-o-diphenyl compound, which, in addition, melts 12° higher. Warm nitric acid vigorously attacks the solid, with evolution of carbonic anhydride and formation of sulphuric acid; water added to the solution precipitates a pale yellow, amorphous nitro-derivative, which dissolves in warm alcohol; if this solution is mixed with excess of alkali, a clear, rich, orange-red coloration appears.

a-Orthotolyl-c-methylphenylthiobiuret.—Orthotoluidine gave a solid which, on recrystallisation from alcohol containing a little benzene, formed shining needles (or, by slow evaporation, thick, vitreous prisms) insoluble in water, easily soluble in hot spirit, and melting at 108° (corr.).

0.2218 gave 0.1743 BaSO₄. S = 10.8. $C_{16}H_{17}N_8SO$ requires S = 10.71 per cent.

With lead and silver salts, it behaves like the phenylic homologue. a-Paratolyl-c-methylphenylthiobiuret.—Paratoluidine, dissolved in absolute alcohol, was used; the solid product, when twice recrystallised from a mixture of benzene and alcohol, occurred in white, glistening plates, melting at 156—157° (corr.).

0.2048 gave 0.1634 BaSO₄. S = 10.97. Calculated S = 10.71 per cent.

The compound is insoluble in water, rather sparingly soluble in hot alcohol, much more easily in benzene. Like the preceding, it is desulphurised by lead and silver salts, and if left in contact with nitric acid, a violent action soon sets in, with formation of a nitro-compound.

a-Methyl-c-methylphenylthiobiuret.—Prepared like the corresponding a-methyl-c-diphenyl compound, the mixture solidifying after a week; by treatment with animal charcoal, colourless, leafy crystals were obtained having a pearly lustre, and melting at 90—91° (corr.).

0.2018 gave 0.2121 BaSO₄. S = 14.45. $CH_8 \cdot N(C_6H_5) \cdot CO \cdot NH \cdot CS \cdot NH \cdot CH_8$ requires S = 14.36 per cent.

The substance is insoluble in water, very freely soluble in hot alcohol, and easily so in cold; its solution gives no precipitate when treated with silver nitrate, but the mixture is blackened on boiling. With the ammoniacal nitrate, silver sulphide is precipitated in the cold, but the solution is not desulphurised by alkaline lead tartrate, even on boiling.

c-Methylphenylthiobiuret. - A trifle less than the calculated quantity of

alcoholic ammonia was used; the yellowish, crystalline product amounted to about 61 per cent. of the theoretical. From hot alcohol, it was deposited in very brilliant, colourless, apparently clinorhombic prisms melting at 166—167° (corr.).

0.2044 gave 0.2348 BaSO₄. S = 15.79.

0.4 gave, by wet combustion, 0.7563 CO₀. C = 51.56.

 $CH_s \cdot N(C_sH_s) \cdot CO \cdot NH \cdot CS \cdot NH_s$ requires S = 15.32; C = 51.62 per cent.

The compound is insoluble in water, easily soluble in hot alcohol. moderately in cold; its solution is neutral to litmus. It is desulphurised in the cold by ammoniacal silver nitrate, and, on heating, by the neutral nitrate or alkaline tartrate of lead.

Action of Chloracetic Acid.—Methylphenylthiobiuret and chloracetic acid were carefully fused together until hydrogen chloride ceased to escape, when the mass solidified. The yellow product was dissolved in hot spirit, potash added until exactly neutral, and the crystals which separated on cooling, after further recrystallisation from a mixture of chloroform and alcohol, were obtained as a yellowish, sandy powder, softening a little at 187°, and melting at 199-200° (corr.), with effervescence, to a liquid the colour of bromine.

0.2032 gave 0.1892 BaSO₄. S = 12.96.

$$CH_8 \cdot N(C_6H_5) \cdot CO \cdot N \cdot C < \frac{S - CH_2}{NH \cdot CO}$$
 requires $S = 12.87$ per cent.

n-Methylphenylcarbamylthiourantoin is insoluble in water, rather sparingly soluble in alcohol, more freely in chloroform. easily in concentrated hydrochloric acid or in dilute caustic alkali; the latter solution is not desulphurised by boiling with a lead salt. but if boiled alone for a few minutes, gives the iron reaction for thioglycollic acid. Ammoniacal silver nitrate gives no precipitate with the alcoholic solution, neither is the mixture blackened on heating.

In the hope of obtaining methylphenylcarbamyldioxythiazole, NMePh·CO·N:O S·CH₂, the above compound was boiled in hydro-

chloric acid solution; decomposition, however, seemed to occur, and the product, when mixed with caustic alkali, yielded ammonia, together with a dark-coloured oil smelling of methylaniline.

a-Methylphenylcarbamyl-β-phenylthiosemicarbazide, --Heat was evolved on adding the hydrazine (in alcohol), and after some days tufts of needles began to appear; these were collected, washed thoroughly with spirit, and the melting point taken; it proved to be 119-120°, and the fused material, on being heated to 140°, showed no sign of change. The whole crop was dissolved in alcohol, a trace of hydrochloric acid added, and the mixture boiled for a short time; on cooling,

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long, brilliant, vitreous prisms melting at 120—121° (corr.) separated, and the mother liquor deposited another crop, melting only 1° lower. It would seem, therefore, that stereoisomeric forms are not produced in this interaction, at least under the above conditions.

0.2034 gave 0.176 BaSO₄. S = 10.72. $CH_3 \cdot N(C_6H_5) \cdot CO \cdot NH \cdot CS \cdot NH \cdot NH \cdot C_6H_5$ requires S = 10.68 per cent.

It is insoluble in water, moderately soluble in hot alcohol, rather sparingly in cold; its alcoholic solution, when boiled with alkaline lead tartrate, is not desulphurised, but develops a pale yellow coloration; alcoholic silver nitrate affords a yellowish precipitate, changing gradually, through orange and brown, to black. Copper sulphate yields an intense, bottle-green coloration; potassium ferricyanide produces no definite effect, but the solution becomes clear, bright orange if treated with bleaching powder, chlorine water, or ferric chloride.

Benzylic a-Methylphenyl-β-thicallophanate.—The constituents, after heating on the water-bath, gave an oily product, which, at the end of three weeks, began to solidify. After frequent recrystallisations from spirit, using animal charcoal, vitreous prisms were obtained, apparently rhombohedral, and melting at 90—91° (corr.).

0.216 gave 0.1704 BaSO₄. S = 10.84. $CH_8 \cdot N(C_6H_5) \cdot CO \cdot NH \cdot CS \cdot O \cdot CH_2 \cdot C_6H_5$ requires S = 10.68 per cent.

The substance is insoluble in water, easily soluble in alcohol; its solution is not affected by heating with alkaline lead tartrate, and with ammoniacal nitrate of silver yields a white precipitate which dissolves on warming.

Attempt to isolate the Thiocarbimids.—About 20 grams of chloride were converted into thiocarbimide, and the solution distilled under a pressure of 12 mm.; nearly all the cumene came over at 56-61°, and between 65° and 68° two very trifling fractions were taken, consisting mainly of cumene also; at this point, distillation practically ceased, the residue now beginning to decompose, with evolution of so much gas that the vacuum, at 95°, could not be kept below 45 mm. The temperature was pushed to 120°, but only 1 or 2 drops of an oily liquid distilled over, and brown fumes now began to appear, whereupon the process was stopped; only a few grams of a reddish-black tar remained, and this eventually hardened; it was found to be practically free from sulphur. The thiocarbimide was not completely destroyed, since all the fractions gave a reaction, more or less, with lead and silver salts; but it is evident that if it can be isolated at all in this way, it must be done at a much lower pressure than 12 mm. In preparing these compounds, it has frequently been noticed that the best yield is obtained when the chlorine is removed in the shortest time; if, for

example, a second heating with mercuric thiocyanate be required, the yield falls below the average; hence it seems probable that, when prepared in the above way, the temperatures of formation and decomposition (even in presence of much solvent) overlap to some extent.

Methylphenylcarbamic Chloride and Thiocarbanilide.—It was hoped that these substances would interact so as to afford a methyltriphenylthiobiuret.

 $NMePh\cdot COCl + NHPh\cdot CS\cdot NHPh = NMePh\cdot CO\cdot NPh\cdot CS\cdot NHPh + HCl.$

On gently heating the substances together, in molecular proportion, the mixture first liquefied, then effervesced, and soon became almost solid; the escaping gas rendered lime-water turbid, and blackened alkaline lead paper, whilst the pasty residue smelt of phenylthiocarbimide. By distilling the residue with steam, it was ascertained that, for every 2 mols. of thiocarbanilide employed, 1 mol. of phenylthiocarbimide was produced. The solid left in the distilling flask was almost entirely soluble in boiling water, and when twice recrystallised from this solvent, formed white prisms, darkening and melting at about 238° (uncorr.). On further examination, it proved to be the hydrochloride of a base, melting at 144-144.5°, giving a picrate melting at 177-178°, and having the properties of sym-triphenylguanidine.

0.2022 gave 25 c.c. moist nitrogen at 14° and 773 mm. N = 14.79. $(NH \cdot C_6H_5)_9C:N \cdot C_6H_5$ requires N = 14.67 per cent.

III. Derivatives of Ethylphenylcarbamyl Isothiocyanate.

This compound was prepared as before, using ethylphenylcarbamic chloride, and the product, a clear, pale brown solution, resembled its congeners.

a-Phenyl-c-ethylphenylthiobiuret.—When the solvents evaporated, a viscid, dark brown oil was left, from which crystals very slowly separated. When purified, they formed white prisms, melting at 106-107° (corr.). The yield was poor.

0.2034 gave 0.1578 BaSO₄. S = 10.66.

 $C_9H_5 \cdot N(C_9H_5) \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_9H_5$ requires S = 10.71 per cent.

The compound is insoluble in water, easily soluble in hot, moderately in cold, alcohol. In its behaviour with silver salts, it resembles the isomeric c-diphenyl-a-ethyl derivative, but differs from this by melting more than 30° lower, and by giving up its sulphur to alkaline lead tartrate.

a-Orthotolyl-c-ethylphenylthiobiuret .-- This was precipitated by light

petroleum as a solid which crystallised from alcohol in pure white needles, resembling the preceding compound in regard to solvents, and melting at 124—125° (corr.). In this case, also, the yield was small. It is desulphurised by lead and silver salts, and is attacked by strong nitric acid in the same way as the o-diphenyl analogue.

0.2018 gave 0.1543 BaSO₄. S = 10.51. $C_{17}H_{10}N_{8}SO$ requires S = 10.23 per cent.

a-Paratolyl-c-ethylphonylthiobiurst.— When recrystallised from a mixture of chloroform and alcohol, it formed slender, white needles, becoming extraordinarily electrical on friction, and melting at 174° (corr.).

 $0.226 \text{ gave } 0.1688 \text{ BaSO}_4$. S = 10.26. Calculated, S = 10.23 per cent.

It is insoluble in water, very slightly soluble in alcohol, benzene, or acetic acid, easily in chloroform.

c-Ethylphenylthiobiurst.—Exactly 1 mol. prop. of alcoholic ammonia was used, and a mass of thick crystals obtained, the yield being over 69 per cent. of the theoretical; when purified by several recrystallisations from spirit, large, flat pointed prisms were obtained, having a greasy lustre, and melting at 147—148° (corr.).

0.211 gave 0.2222 BaSO₄. S = 14.47. $C_2H_5 \cdot N(C_6H_5) \cdot CO \cdot NH \cdot CS \cdot NH_2$ requires S = 14.36 per cent.

It is insoluble in water, easily soluble in hot alcohol, but only slightly in cold.

n-Ethylphenylcarbamyl-thiourantoin.—Obtained by fusing the above compound with monochloracetic acid, and operating as previously described. After treatment with animal charcoal and two recrystallisations from a mixture of chloroform and alcohol, the product formed a sandy powder, still slightly yellow; it sintered at 182° and melted at 184—185° (corr.) to a deep red liquid.

0.2009 gave 0.1865 BaSO₄. S=12.76.

 $C_2H_5\cdot N(C_6H_5)\cdot CO\cdot N:C < \frac{S-CH_2}{NH\cdot CO}$ requires $S=12\cdot 17$ per cent.

The solution in caustic alkali, when boiled for a few minutes, gives the iron reaction for thioglycollic acid; with respect to solvents, and to lead and silver salts, this compound resembles the *n*-methylphenyl homologue.

Benzylic a-Ethylphenyl-β-thioallophanats.—Obtained at the temperature of the water-bath; when purified, it formed small, vitreous prisms, free from colour and melting at 119.5—120.5° (corr.).

Found, S = 10.13; C = 64.87 per cent. $C_2H_5 \cdot N(C_6H_5) \cdot CO \cdot NH \cdot CS \cdot O(CH_2 \cdot C_6H_5)$ requires $S = 10 \cdot 20$; C = 64.92 per cent.

It is insoluble in water, moderately soluble in hot alcohol; the solution in benzene is precipitated by adding light petroleum; it is not desulphurised by alkaline lead salts; nitrate of silver yields a white precipitate which dissolves in ammonia on warming,

IV. Derivatives of Benzylphenylcarbamyl Isothiocyanate.

The parent compound formed a yellow solution having no distinctive odour; with ferric chloride, it gave a slight thiocyanic reaction, and otherwise resembled its congeners.

a-Phenyl-c-benzylphenylthiobiuret.—Colourless prisms, insoluble in water, easily soluble in hot alcohol, and melting at 102.5—103.5°(corr.).

 $C_7H_7\cdot N(C_6H_5)\cdot CO\cdot NH\cdot CS\cdot NH\cdot C_6H_5$, requires Found, 8=8.75. S = 8.87 per cent.

It is isomeric with the a-benzyl-c-diphenyl compound melting at 168°, from which it also differs by giving up its sulphur to alkaline lead tartrate.

a-Orthotolyl-c-benzylphenylthiobiuret. - The crude product, the yield of which amounted to over 72 per cent. of the theoretical, after recrystallisation from a mixture of alcohol and chloroform and then from spirit alone, formed brilliant, vitreous lozenges, only moderately soluble in boiling alcohol, easily in chloroform, and melting at 131-132° (corr.). It is desulphurised in the cold by neutral or ammoniacal silver nitrate, and by alkaline lead salts on boiling. With nitric acid, it gives a canary-yellow solid, whose alcoholic solution acquires a fine ruby colour when mixed with excess of alkali.

Found, S = 8.60. $C_{22}H_{21}N_8SO$ requires S = 8.54 per cent.

Desulphurisation.—By desulphurising certain of the thiobiurets described in this paper, a number of corresponding biurets have been obtained, a complete account of which is deferred for the present; the compound mentioned below was got by chance in one of these preparations, owing to the incautious use of ammonia, and is here introduced in order to show that the substituted carbamyl group may also take part in the formation of a guanidine derivative.

The orthotolyl compound, dissolved in boiling alcohol with the assistance of a little caustic potash, was mixed with alcoholic ammonia and treated with the calculated quantity of ammoniacal silver nitrate; the metallic sulphide was filtered off, and the filtrate precipitated by The solid product, when recrystallised a few times from

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alcohol, occurred in well-formed, hard, vitreous prisms insoluble in water, easily soluble in hot alcohol, melting at $136-136\cdot5^{\circ}$ (corr.) yielding $15\cdot39$ per cent. of nitrogen, and hence not consisting of the expected biuret, $C_7H_7\cdot NPh\cdot CO\cdot NH\cdot CO\cdot NHoTo$, which would require $N=11\cdot73$ per cent.

A complete combustion gave the following data.

0.2042 gave 0.55 CO_2 and 0.1216 H_2O . C=73.45; H=6.6. 0.2011 , 26.8 c.c. moist nitrogen at 15° and 767 mm. N=15.81.

These figures lead to the formula C₂₂H₂₂N₄O.

• Consequently, the ammonia, which was added merely to hinder the precipitation of silver oxide, itself takes part in the change, the product being a benzylphenylcarbamylorthotolylguanidine,

$$C_7H_7 \cdot NPh \cdot CO \cdot NH \cdot CS \cdot NHTo + 2AgNO_3 + NH_3 = C_7H_7 \cdot NPh \cdot CO \cdot NH \cdot C(NH) \cdot NHTo + Ag_2S + 2HNO_3.$$

a-Methyl-c-benzylphenylthiobiuret.—White prisms, melting at 99—100° (corr.); insoluble in water, moderately soluble in hot alcohol; desulphurised by ammoniacal silver nitrate in the cold. Alkaline lead tartrate gives a white precipitate, easily soluble in excess of warm, dilute alkali; this solution is not perceptibly affected by boiling.

S found, 10.97. $C_{16}H_{17}N_8SO$ requires S = 10.71 per cent.

a-Ethyl-c-benzylphenylthiobiuret.—The product was dark coloured and sticky; after standing for about 6 weeks, it began to solidify, and eventually yielded white, pointed prisms, moderately soluble in cold alcohol, easily in benzene, and melting at 67—68°.

Found, S = 10.35. $C_{17}H_{19}N_3SO$ requires S = 10.26 per cent.

Its properties are similar to those of the preceding compound.

c-Benzylphenylthiobiuret.—Was deposited from a mixture of chloroform and alcohol in beautiful, vitreous, apparently rectangular, prisms, becoming slightly moist at 178° and melting at 179—180° (corr.) with effervescence.

Found, S = 11.47. $C_6H_5 \cdot N(C_7H_7) \cdot CO \cdot NH \cdot CS \cdot NH_2$ requires S = 11.24 per cent.

Properties: rather sparingly soluble in hot alcohol, more readily in chloroform; it dissolves easily in warm, dilute alkali, and the solution is desulphurised by boiling with lead tartrate. Neutral silver nitrate gives no precipitate; the ammoniacal nitrate yields a

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white, curdy derivative, which is stable in the cold, but dissolves partially on warming, the solution soon becoming black. Nitric acid gives a yellow nitro-compound.

n-Benzylphenylcarbamylthiourantoin.—Prepared like its analogues; when twice recrystallised, it was a yellowish, sandy powder softening at 193° and melting between 194° and 195° (corr.) to a deep red liquid. It gives the iron reaction for thioglycollic acid when boiled with potash, and generally resembles the corresponding n-methylphenyl compound.

Found,
$$S = 9.75$$
. $C_6H_5 \cdot CH_2 \cdot N(C_6H_5) \cdot CO \cdot N \cdot C < S - CH_2$ requires $S = 9.85$ per cent.

Benzylic a-Benzylphenyl-β-thicallophanate.—Sixty-five per cent. of the theoretical yield was obtained; on recrystallisation from a mixture of alcohol and chloroform, and finally from alcohol alone, the product was obtained in brilliant, vitreous prisms, melting at 133—134° (corr.) to a dark liquid.

Found, S = 8.58. $C_{22}H_{20}N_2SO_2$ requires S = 8.52 per cent.

In regard to solvents, &c., it resembles its congeners already described.

V. Phenyloxamyl (Oxanilyl) Isothiocyanate.

A solution of this compound was obtained by heating phenyloxamic chloride, dissolved in anhydrous toluene, with excess of lead thiocyanate; * the temperature must not be allowed to rise too high, otherwise decomposition sets in, with brisk evolution of gas. The solution, when cooled thoroughly and filtered, was clear reddish-brown in colour, free from halogen, possessed no characteristic odour, and gave, with lead and silver salts, the usual thiocarbimidic reactions. When shaken up with cold water, the mixture gave a slight red coloration with ferric chloride, and on heating with water, the thiocyanic reaction, although not intense, was appreciably increased.

The interaction which it was desired to realise between lead thiocyanate and oxanilic chloride runs as follows.

$$2NHPh\cdot CO\cdot COCl + Pb(SCN)_2 = PbCl_2 + 2NHPh\cdot CO\cdot CO\cdot NCS$$

It was quite possible, of course, that the NCS-group, if formed, might unite with the hydrogenised residue, NHPh, so as to produce some ring compound, such as phenylthioparabanic acid, CS NH--CO

^{*} The mercury salt gave less satisfactory results, owing to its tendency to produce some soluble, amorphous, metallic compound.

On the other hand, the power of NCS to combine with an amidic residue is paralysed, or at least greatly weakened, if the latter be in direct union with an acidic group; * it therefore appeared probable that NHPh·CO·CO·NCS would be able to exist as such, and in effect this proved to be the case, for the compound exhibits the 'unsaturated' thiocarbimidic character, uniting directly with aniline to form a thiocarbamide.

Action of Aniline.—When the pure base (1 mol.) was dissolved in absolute alcohol and mixed with aniline, the mixture soon became hot, and a finely-divided, crystalline solid was deposited, which, on recrystallisation from a mixture of benzene and alcohol, formed microscopic needles having a lemon-yellow colour, which was not removed by treatment with animal charcoal; it melted at 172—173° (corr.).

0.2200 gave 0.1732 BaSO₄. S=10.82. 0.2072 ,, 25 c.c. moist nitrogen at 20° and 765 mm. N=14.00. $C_6H_5\cdot NH\cdot CO\cdot CO\cdot NH\cdot CS\cdot NH\cdot C_6H_5$ requires S=10.71; N=14.08 per cent.

The product, a-phenyloxamyl-b-phenylthiocarbamide, or diphenylthio-oxaluramide, is insoluble in water or hydrochloric acid, moderately soluble in hot alcohol or acetone, more easily in benzene, very freely in chloroform. The alcoholic solution is desulphurised in the cold by ammoniacal silver nitrate, and by warming with alkaline lead tartrate; with ferric chloride, it gives no coloration, either directly or after previous heating with alkali. The solid dissolves gradually in hot caustic potash, and if the solution is now mixed with a slight excess of hydrochloric acid, phenylthiourea is precipated.

Action of Ammonia.—On passing excess of the gas into the toluene solution, a solid was precipitated which, after recrystallisation from spirit, was obtained in pearly, flattened crystals practically devoid of sulphur and melting at about 223°; the mother liquor, from which the solid had been deposited, contained thiocyanic acid. The crystals, which were not analysed, consisted, probably, of phenyloxamide, the melting point of which is 224°.

 $NHPh\cdot CO\cdot CO\cdot NCS + NH_3 = HSCN + NHPh\cdot CO\cdot CO\cdot NH_2$

In conclusion, the author desires to acknowledge his indebtedness to the Research Fund Committee for a grant in aid of the purchase of materials used in the above investigation; and to Mr. R. E. Doran, for assistance rendered in connection with it.

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^{*} Phenylthiocarbimide does not interact, under ordinary circumstances, with acetamide or acetanilide; it does not even seem able to combine with asparagine.

XXXIX.—Formation of a-Pyrone Compounds and their Transformation into Pyridine Derivatives.

By SIEGFRIED RUHEMANN.

In my last communication (this vol., p. 245) to the Society, I described a method of formation of α -pyrone compounds which is based on the action of sodium ethoxide on a mixture of the ethylic salts of a β -ketonic acid, and of an acid containing an acetylene linking, ethylic phenylpropiolate being used along with ethylic acetoacetate and ethylic benzoylacetate. A further study of this reaction led to the result that β -diketones, under the influence of sodium ethoxide, also condense with ethylic phenylpropiolate yielding α -pyrone derivatives of the general formula $C_6H_5 \cdot C \subset CH - CO$.

(R and R' denoting hydrocarbon radicles).

The formation of these compounds may be explained by assuming that, in the first phase of the reactions, the ethylic salt of an unsaturated ketonic acid is produced which then loses alcohol and condenses to the α -pyrone derivative. In the case of the interaction of ethylic phenylpropiolate and acetylacetone, these two phases may be expressed by the equations

$$C_{6}H_{5} \cdot C : C \cdot COOC_{2}H_{5} + CH_{3} \cdot CO \cdot CH_{2} \cdot CO \cdot CH_{3} = C_{6}H_{5} \cdot C \cdot COOC_{2}H_{5} = C_{2}H_{5} \cdot OH + C_{6}H_{5} \cdot C \cdot COOC_{2}H_{5} = C_{2}H_{5} \cdot OH + C_{6}H_{5} \cdot C \cdot CH_{2} \cdot CO \cdot CH_{3} = CO \cdot CH_{3} \cdot CH_{3}$$

The process really does take place in this manner, for the ethylic salt of the unsaturated diketonic acid occurring in this equation can be isolated, and the presence of the intermediate product of the reaction, that is, the ethylic salt of an unsaturated ketonic acid, is also indicated by the fact that the high boiling fractions of the product formed on digesting a mixture of ethylic phenylpropiolate and the ethylic salt of a β -ketonic acid with sodium ethoxide yield a violet coloration with ferric chloride.

Alcoholic ammonia, as I mentioned in my previous paper, reacts with ethylic phenylmethyl-a-pyronecarboxylate with formation of an additive compound; it behaves, therefore, like ethylic isode-hydracetate. The constitution of the product which is thus formed from the latter substances is, according to Anschütz, Bendix, and Kerp (Annalsn, 1890, 259, 148), probably represented by the formula

$$\mathbf{CH_8 \cdot C} \underbrace{\overset{\mathbf{C \cdot (COOEt) \cdot C(CH_3) : CH}}_{\mathbf{C}(\mathbf{NH_2}) \cdot \mathbf{ONH_4} \cdot \mathbf{C}(\mathbf{NH_2}) \cdot \mathbf{ONH_4}}_{\mathbf{C}(\mathbf{NH_2}) \cdot \mathbf{ONH_4}}_{\mathbf{C}(\mathbf{NH_2}) \cdot \mathbf{ONH_4}}$$

An analogous structure would have to be assigned to the ammonium compound which I obtained from the former a-pyrone derivative. This view as to the constitution of the additive products would, indeed, account for the ease with which they lose ammonia and are reconverted into the a-pyrone compounds. On the other hand, the expression

$$\mathbf{CH_{s}C} \underbrace{ \begin{matrix} \mathbf{C}(\mathbf{COOEt}) \cdot \mathbf{C}(\mathbf{C_{b}H_{b}}) \\ \mathbf{NH_{o}} \end{matrix} }_{\mathbf{COONH_{A}}} \mathbf{COONH_{A}}$$

would be in accordance with the results at which Nieme and v. Pechmann (Annalen, 1891, 261, 190) arrived in the course of their research on coumalic acid, and especially with those of Guthzeit and Dressel (Annalm, 1891 262, 89) on the action of ammonia on ethylic ethoxya-pyronedicarboxylate. Moreover, the transformation of the above ammonium salt into the pyridine derivative can readily be explained by means of this formula. The method employed is, indeed, founded on it, consisting as it does in the substitution of the ethyl radicle for the ammonium group, and the distillation of the ethylic salt thus formed. This reaction has also been successfully applied to the preparation of ethylic diphenylpyridonecarboxylate from the ethylic salt of diphenyl-a-pyronecarboxylate. It may be pointed out that the latter is partially changed into the pyridone derivative if left in contact with alcoholic ammonia, whereas the former a-pyrone compound is not changed. These facts, together with the results obtained by other workers, indicate that the readiness with which the formation of pyridine derivatives takes place is determined by the negative character of the radicle in the a'-position of the a-pyrone compound.

EXPERIMENTAL

Ethylic a-hydroxy-a'-methyl-y-phenylpyridine-\beta'-carboxylate,

For the preparation of this substance, ethylic phenylmethyl-a-pyronecarboxylate is transformed by alcoholic ammonia into its additive compound, and the silver salt prepared from this is dried in a vacuum, and digested with ethylic iodide on the water-bath; after the removal of the excess of ethylic iodide, the residue is extracted with ether, and the ether evaporated, when a yellowish oil is left which does not solidify. If, however, the silver salt is not perfectly dry, crystals separate from the oily product, which are identical with the original

a-pyrone derivative; their formation can only be due to hydrolysis of the ethylic salt first formed, and the subsequent removal of ammonia. This conclusion is substantiated by the fact that in this case ammonia is evolved. The oil cannot be purified by distillation, as it decomposes with loss of 1 mol. alcohol and formation of ethylic phenylmethylpyridonecarboxylate, the latter passing over at about 270° under a pressure of 10 mm. as a yellowish, gummy product; this is soluble in alcohol, from which it crystallises in colourless needles, melting at 184°, and sparingly soluble in ether, but readily in alcohol. The oil was analysed, with the following results.

0.2040 gave 0.5233 CO_2 and 0.1095 H_2O . C = 69.95; H = 5.96. 0.2458 ,, 11.5 c.c. of nitrogen at 15° and 756 mm. N = 5.45. $C_{15}H_{15}NO_3$ requires C = 70.0; H = 5.83; N = 5.44 per cent.

The pyridone derivative dissolves both in potash and hydrochloric acid, and thus exhibits both acidic and basic properties. In alcoholic solution, it gives a yellowish-red coloration with ferric chloride.

Phenylmethylpyridomecarboxylic Acid.—The hydrolysis of the ethylic salt is best brought about by boiling its solution in concentrated potash in a reflux apparatus for 2—3 hours; on adding hydrochloric acid, a white, crystalline powder is precipitated which dissolves with difficulty in alcohol, and crystallises from it in colourless prisms melting at 240° with evolution of carbonic anhydride.

0.2530 yielded 13 c.c. of nitrogen at 13° and 778 mm. N = 6.21. $C_{13}H_{11}NO_3$ requires N = 6.11 per cent.

Phonylmethylpyridons,
$$C_6H_5$$
 CCH—CCOH .—On heating the acid

at 240—245° until carbonic anhydride ceases to be evolved, phenylmethylpyridone is formed; this is readily soluble in rectified spirit, and crystallises from the concentrated solution in colourless needles melting at 207—208°.

0.2013 gave 0.5730 CO₂ and 0.1095 H_2O . C = 77.63; H = 6.04. 0.2272 ,, 15 c.c. of nitrogen at 19° and 768 mm. N = 7.66. $C_{12}H_{11}NO$ requires C = 77.83; H = 5.94; N = 7.56 per cent.

This substance dissolves in dilute potash, and also in hydrochloric acid. On adding platinic chloride to the hydrochloric acid solution, a platinochloride is precipitated in golden-yellow needles which gave the following result on analysis.

0.2744 left, on ignition, 0.0674 platinum. Pt = 24.56. $(C_{12}H_{11}NO)_2, H_2PtCl_6$ requires Pt = 24.92 per cent.

Ethylic a-Hydroxy-γa'-diphenylpyridine-β'-carboxylate,

$$\begin{array}{c|c} C_6H_5\\ C_0CE_t\cdot C & CH\\ C_6H_5\cdot C & \overline{N} & C\cdot OH \end{array}$$

Under the influence of sodium ethoxide, ethylic phenylpropiolate condenses with ethylic benzoylacetate to form diphenyl-a-pyrone-carboxylate (loc. cit.); alcoholic ammonia gradually dissolves this compound, and the yellow solution deposits colourless prisms after some time. The additive product thus formed is less stable than that obtained from ethylic phenylmethyl-a-pyronecarboxylate, as it turns yellow and easily decomposes when kept in a vacuum; even in the air, it loses ammonia, and then does not completely dissolve in cold water until a small quantity of ammonia is added. Copper sulphate added to this solution produces a green precipitate of the corresponding copper salt, resembling those formed from the additive products of ammonia with ethylic isodehydracetate and ethylic phenylmethyl-a-pyronecarboxylate. On adding silver nitrate to the solution of the ammonium compound, a white, flocculent silver salt is thrown down; this was dried in a vacuum and analysed.

0.3948 gave 11.5 c.c. of nitrogen at 15° and 759 mm. N = 3.38.

0.3430 left, on ignition, 0.0830 Ag. Ag = 24.18.

 $C_{20}H_{18}AgNO_4$ requires N = 3.15; Ag = 24.32 per cent.

When the dry silver salt is treated with ethylic iodide, as in the former case, it yields a very viscous, red product which, if heated in a vacuum, loses alcohol and forms ethylic diphenylpyridenecarboxylate; the latter distils at 300—315° with but slight decomposition, under a pressure of about 10 mm., and solidifies as a reddish gum which is only sparingly soluble in ether, and with difficulty in alcohol. From the alcoholic solution, colourless prisms separate which melt at 210°.

0.2017 gave 0.5560 CO₃ and 0.0977 H_2O . C = 75.17; H = 5.38. 0.2603 , 10.5 c.c. of nitrogen at 16° and 747 mm. N = 4.72. $C_{20}H_{17}NO_8$ requires C = 75.23; H = 5.32; N = 4.39 per cent.

With ferric chloride, the alcoholic solution of this ethylic salt gives a yellowish-red coloration. It differs from ethylic phenylmethylpyridonecarboxylate inasmuch as it is not dissolved by hydrochloric acid; the acidic character of this compound, however, is indicated by its solubility in dilute potash.

Ethylic diphenylpyridonecarboxylate, as mentioned in the introduction, is formed directly by the action of alcoholic ammonia on the

a-pyrone compound, and is contained in the filtrate from the additive product. On evaporating the yellow solution, it remains behind; it was recognised by the melting point and the crystalline form.

Formation of a-Pyrone Derivatives from Ethylic Phenylpropiolate and \(\beta\)-Diketones.

The addition of β -diketones to ethylic phenylpropiolate is effected in the same manner as that of the ethylic salts of β -ketonic acids. This reaction has been carried out with acetylacetone and benzoylacetone.

Ethylic γ-Diaceto-β-phenylcrotonate.—On digesting a mixture of equivalent quantities of acetylacetone and ethylic phenylpropiolate with 0.5 gram of sodium ethoxide for 12 hours on the water-bath, and then adding dilute sulphuric acid to the product, an oil is obtained which consists of a mixture of the ethylic salt of diacetophenyl-crotonate, C₆H₅·CCH·COOC₂H₅, with the a-pyrone compound formed from the latter by the loss of alcohol; their separation is effected by distillation under diminished pressure. On repeated fractionation, the former is obtained as a yellow, highly refractive oil boiling at 193—195° under a pressure of 10 mm.; in alcoholic solution, it gives a deep red coloration with ferric chloride. On analysis, the following

0.2050 gave 0.5273 CO₂ and 0.1190 H₂O. C = 70.01; H = 6.45. $C_{16}H_{18}O_4$ requires C = 70.07; H = 6.57 per cent.

results were obtained.

γ-Phenyl-a'-methyl-β'-aceto-a-pyrone, C₆H₅·C—CH·CO—O C(CO·CH₈): C·CH₈ The fraction of the oil which distils between 210° and 220° under a pressure of 10 mm. solidifies almost completely; the solid dissolves readily in hot alcohol and, on cooling, crystallises in colourless, prismatic plates which melt at 128°.

0.2055 gave 0.5540 CO₂ and 0.0975 H₂O. C = 73.52; H = 5.27. $C_{14}H_{12}O_3$ requires C = 73.68. H = 5.26 per cent.

Absolute alcoholic ammonia dissolves this substance if left in contact with it for 1-2 hours, and the yellow solution, which does not deposit crystals if left for a day, undoubtedly contains the additive compound of the α -pyrone derivative with 2 mols. NH₃, for on evaporation in a vacuum a solid residue is left which dissolves in cold water containing a little ammonia, and with silver nitrate, the solution yields a white silver salt, $C_{14}H_{12}AgNO_3$. This salt was dried in a vacuum and analysed.

0.3082 left on ignition 0.0937 Ag. Ag = 30.40.

0.3007 , , , 0.0918 Ag. Ag = 30.52.

0.3520 gave 13.5 c.c. of nitrogen at 20° and 745 mm. N=4.27.

 $C_{14}H_{12}AgNO_3$ requires Ag = 30.68; N = 3.97 per cent.

Phenylbenzoylmethyl-a-pyrone or Diphenylacetyl-a-pyrone.—On using benzoylacetone, instead of acetylacetone, along with ethylic phenyl-propiolate, the corresponding a-pyrone derivative is formed, and can be isolated from the product by fractional distillation. The distillate, which passes over between 260° and 270° under a pressure of about 12 mm., solidifies, and crystallises from alcohol in thick, colourless prisms melting at 143—144°.

0.1986 gave 0.5720 CO₂ and 0.0872 H₂O. C=78.54; H=4.87. $C_{19}H_{14}O_{3}$ requires C=78.62; H=4.83 per cent.

The constitution of this substance is to be represented by one of the two formulæ,

$$C_6H_5 \cdot C \leftarrow C(CO \cdot C_6H_5) \cdot C \cdot CH_8$$
 or $C_6H_5 \cdot C \leftarrow C(COCH_8) \cdot C \cdot C_6H_5$ of which the latter seems the more probable.

With alcoholic ammonia, it forms an additive compound which remains in solution; the crystalline solid which is left on evaporation, is reconverted into the a-pyrone derivative on adding hydrochloric acid to its aqueous solution.

The silver salt prepared from the ammonium compound, after being dried in a vacuum, was analysed, with the following result.

0.3798 left on ignition 0.0988 Ag.
$$Ag = 26.01$$
.
 $C_{10}H_{16}AgNO_8$ requires $Ag = 26.08$ per cent.

Experiments are in progress to effect the transformation of the α -pyrone derivatives produced from the β -diketones into the corresponding pyridine compounds, by the same method as that employed to effect a similar change in the case of the compounds obtained from the ethylic salts of β -ketonic acids. I intend, also, to examine the action of substituted ammonias on the α -pyrone compounds described in this paper, and hope to lay the results before the Society in a short time.

GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.



XL.—Hydrolysis of the γ-Cyanides of Di-substituted Acetoacetates.

By WILLIAM TREVOR LAWRENCE.

In a note in the Proceedings of the Chemical Society, 1898, p. 251, I suggested that the action of hydrochloric acid on methylic γ -cyanodimethylacetoacetate produced an acid of the formula

COOH·CH:C(OH)·C(CH₈)₂·COOH,

but at the same time doubts were expressed as to the correctness of this supposition, as the acid was not acted on by nitric acid, sulphuric acid, or potassium permanganate, and did not give a coloration with ferric chloride. It was suggested to me by a colleague that the substance was probably a lactonic acid, and this view of its constitution has been adopted by Conrad and Gast (Ber., 1899, 32, 137), who represent the reaction by the following equations.

$$\begin{split} \mathbf{CN} \cdot \mathbf{CH} &: \mathbf{C}(\mathbf{OH}) \cdot \mathbf{C}(\mathbf{CH}_{s})_{2} \cdot \mathbf{COOCH}_{s} + \mathbf{H}_{2}\mathbf{O} \\ &= \mathbf{CN} \cdot \mathbf{CH}(\mathbf{OH}) \cdot \mathbf{CH}(\mathbf{OH}) \cdot \mathbf{C}(\mathbf{CH}_{s})_{2} \cdot \mathbf{COOCH}_{s} \\ &= \mathbf{CN} \cdot \mathbf{CH}(\mathbf{OH}) \cdot \mathbf{C}(\mathbf{CH}_{s})_{2} \cdot \mathbf{COOCH}_{s} + 2\mathbf{H}_{2}\mathbf{O} + \mathbf{HCl} \\ &= \mathbf{COOH} \cdot \mathbf{CH} \cdot \mathbf{CH}(\mathbf{OH}) \cdot \mathbf{C}(\mathbf{CH}_{s})_{2} + \mathbf{NH}_{4}\mathbf{Cl} + \mathbf{CH}_{s} \cdot \mathbf{OH}. \\ &= \mathbf{COOH} \cdot \mathbf{CH} \cdot \mathbf{CH}(\mathbf{OH}) \cdot \mathbf{C}(\mathbf{CH}_{s})_{2} + \mathbf{NH}_{4}\mathbf{Cl} + \mathbf{CH}_{s} \cdot \mathbf{OH}. \end{split}$$

The acid is, therefore, the lactone of aa-dimethyl-a'β-dihydroxyglutaric acid; this acid is easily reduced by hydriodic acid forming the lactone of aa-dimethyl-a'-hydroxyglutaric acid, but I have been unable to further reduce it to aa-dimethylglutaric acid, the synthesis of which formed the original object of this research.

Methylic aa-dimethyl- γ -cyanacetoacetate, when dissolved in alcohol and treated with dry hydrogen chloride, is converted into a chlorinated ethereal salt,

$$\begin{split} & \textbf{CN} \cdot \textbf{CH} \cdot \textbf{C}(\textbf{OH}) \cdot \textbf{C}(\textbf{CH}_8)_2 \cdot \textbf{COOCH}_8 + 2\textbf{C}_2\textbf{H}_5 \cdot \textbf{OH} + 3\textbf{HCl} \\ &= \textbf{COOC}_2\textbf{H}_5 \cdot \textbf{C}(\textbf{OH}_8)_2 \cdot \textbf{CH}(\textbf{OH}) \cdot \textbf{CHCl} \cdot \textbf{COOC}_2\textbf{H}_5 + \textbf{NH}_4\textbf{Cl} + \textbf{CH}_8\textbf{Cl}. \end{split}$$

Ethylic aa-dimethyl-\$\beta\$-hydroxychloroglutarate can be reduced by sodium amalgam, and this reduction seems to be the best method of obtaining aa-dimethylglutaric acid; but as Conrad and Gast (loc. cit.) wish to reserve to themselves the further investigation of these compounds (and here I must express my regret at having overlooked a passage to this effect in a previous paper of theirs on another subject: Ber., 1898, 31, 1339), I shall content myself by publishing the results I have obtained.

Methylic Dimethylcyanacetoacetate, $CN \cdot CH:C(OH) \cdot C(CH_8)_2 \cdot COOCH_3$.

To 50 grams of methylic y-bromodimethylacetoacetate* dissolved in an equal weight of dry ether, 25 grams of finely powdered potassium cyanide (98 per cent.) are added, and the mixture heated on the water-bath with occasional shaking for 4 hours; it is then filtered from the potassium bromide and unchanged cyanide by aid of the pump, treated for another 4 hours with a fresh portion of cyanide, and again filtered. The ethereal solution, after being washed with water and sodium carbonate solution, is dried over anhydrous sodium sulphate, and on distilling off the ether a limpid oil is obtained which generally contains no unchanged bromide, and can be converted directly into the acid. The yield of nitrile is 85 to 90 per cent. of the theoretical, and the method is consequently more advantageous than that of Conrad and Gast; their nitrile, moreover, could not be obtained free from bromide. If the oil is submitted to fractional distillation, the greater portion passes over between 126° and 128° under a pressure of 18 mm.

Methylic γ -cyanodimethylacetoacetate smells strongly of hydrocyanic acid, and gives a yellow coloration with ferric chloride; it does not react with phenylhydrazine \dagger in the cold, or with semicarbazide. It appears, however, to give a sodium compound, and with zinc turnings, in the presence of a trace of ethylic bromacetate, it yields a solid, white zinc salt analogous to the compound formed from ethylic acetonedicarboxylate under similar circumstances. Endeavours were first made to etherify the cyano-group by dissolving the cyanacetoacetate in absolute alcohol and passing dry hydrogen chloride into the solution, but the oily product invariably contained chlorine and traces of nitrogen; by repeated fractionation under diminished pressure, however, an oil was obtained free from nitrogen, and dis-

* The ethereal salt used in the preparation of this substance was obtained from a German firm as the ethylic salt, but an analysis and the boiling point showed that it was the methylic salt; the methyl groups had been introduced into ethylic acetoacetate by the use of sodium methoxide, and consequently the ethylic salt was converted into the methylic salt.

Pure methylic dimethylacetoacetate should give no coloration with ferric chloride; a violet colour is obtained, however, if it contains the monomethyl compound, and on bromination the latter is converted into methylic γ -bromomonomethylacetoacetate; this, on distillation, forms tetrinic acid, which crystallises out in the distilling flask.

† If unchanged bromide is present, the mixture becomes hot on the addition of the reagent, and the hydrazine of methylic γ-bromodimethylacetoacetate separates out.

tilling constantly between 148° and 150° under a pressure of 40 mm. On analysis, the oil gave figures corresponding with the empirical formula, $C_{11}H_{12}ClO_5$.

0.2514 gave 0.4622 CO₂ and 0.1463 H₂O. C = 50.14; H = 6.46. 0.2548 , 0.1350 AgCl. Cl = 13.1.

 $C_{11}H_{17}ClO_5$ requires C = 50.00; H = 6.44; Cl = 13.4 per cent.

The chlorinated ethereal salt, on hydrolysis with hydrochloric acid, yields the lactone of dimethyldihydroxyglutaric acid, and probably has the formula of ethylic aα-dimethyl-β-hydroxy-α'-chloroglutarate,

its conversion into the lactone being represented by the equation,

$$\begin{aligned} \text{COOC}_2\mathbf{H}_5 \cdot \text{CHCl} \cdot \text{CH}(\text{OH}) \cdot \text{C}(\text{CH}_3)_2 \cdot \text{COOC}_2\mathbf{H}_5 \\ &= \text{COOC}_2\mathbf{H}_5 \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{C}(\text{CH}_3)_2 + \text{C}_2\mathbf{H}_5 \text{Cl}. \\ \text{O} & \text{COOC}_3\mathbf{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{C}(\text{CH}_3)_2 + \text{C}_3\mathbf{H}_5 \cdot \text{Cl}. \end{aligned}$$

The chlorinated compound, on reduction with sodium amalgam, yields a mixture of acids which are difficult to separate; it is reduced by hydriodic acid to the lactone of dimethylhydroxyglutaric acid. Attempts were also made to reduce methylic cyanodimethylaceto-acetate by means of sodium or aluminium amalgam under varied conditions, but dimethylmalonic acid was invariably produced.

Methylic cyanodimethylacetoacetate is boiled with three times its volume of concentrated hydrochloric acid until the oil has entirely disappeared, which requires about 3 hours. On cooling, most of the lactonic acid separates in well-defined prisms, and the remainder may be recovered from the mother liquor by evaporating to dryness and separating the lactonic acid from the ammonium chloride by means of alcohol or ether. The acid, after recrystallisation from water, was analysed.

0·1367 gave 0·2418 CO₂ and 0·0705 H₂O. C=48·24; H=5·73. 0·1998 , 0·3499 CO₂ , 0·1086 H₂O. C=48·17; H=6·00.
$$C_7H_{10}O_5$$
 requires C=48·27; H=5·75 per cent.

The lactonic acid crystallises from water, melts at 213—214°, and distils without decomposition under diminished pressure; the pure acid obtained by the hydrolysis of the methylic salt melts at 216°. It does not combine with phenylhydrazine or semicarbazide, crystallises

unchanged from concentrated sulphuric acid, and can be boiled with fuming nitric acid without change. It does not decolorise permanganate solution when heated with it at 60°, and with ferric chloride it gives a yellow coloration. It does not combine with bromine.

The acid is also obtained by the action of 50 per cent. sulphuric acid on the nitrile, the hydrolysis being complete after 5 minutes heating. The acid obtained by this method, however, contains a small amount of an acid of lower melting point (the mixture of acids obtained by extracting the sulphuric solution with ether melts at 168°), which, on repeated fractional recrystallisation from dry ether and water, is obtained melting at 96°.

0.1579 gave 0.2827 CO₂ and 0.0331 H₂O.
$$C = 48.7$$
; $H = 5.8$. $C_7H_{10}O_5$ requires $C = 48.3$; $H = 5.75$ per cent.

The analysis shows that the acid of lower melting point has the same empirical formula as the acid melting at 213—214°; it is, possibly, a stereoisomeride, as the lactonic acid contains two asymmetric carbon atoms, marked *.

The yield of the lactonic acid by either method represents 90 per cent. of the theoretical.

The silver salt of the lactonic acid, prepared from silver carbonate and a concentrated aqueous solution of the acid, is obtained in well defined prisms on evaporating the solution over sulphuric acid in a vacuum.

0.2365 gave 0.9020 Ag. Ag =
$$38.1$$
.
AgC₇H₀O₈ requires Ag = 38.4 per cent.

Similar copper and zinc salts were obtained by dissolving the carbonates of these metals in a concentrated solution of the lactonic acid.

Methylic Salt of the Lactone of aa-Dimethyl-a'β-dihydroxyglutaric Acid, COOCH₃·CH·CH(OH)·C(CH₃)₂, obtained by passing hydrogen chloride

into the solution of the lactonic acid in methylic alcohol, is deposited in white crystals on concentrating the solution; it was recrystallised from hot water, in which it is readily soluble.

0.1751 gave 0.3265 CO₂ and 0.1016 H₂O. C=50.86; H=6.44.
$$C_8H_{12}O_5$$
 requires C=51.06; H=6.38 per cent.

It crystallises unchanged from fuming nitric acid, melts at 104°, and distils unchanged at 285°.

Ethylic Salt of the Lactone of aa-Dimethyl-aβ-dihydroxyglutaric Acid, COOC₂H₆·CH·CH(OH)·C(CH₃)₂.—This salt is obtained by boiling the

acid for 3 hours with twice its weight of ethylic alcohol mixed with an equal volume of sulphuric acid; on fractionating the oily product under reduced pressure (18 mm.), the ethylic salt passed over at 169—170° as a thick oil which crystallised after a time. When recrystallised from alcohol it melted at 49°.

0.2768 gave 0.3622
$$CO_2$$
 and 0.1663 H_2O . $C = 53.28$; $H = 6.7$. $C_7H_{14}O_5$ requires $C = 53.5$; $H = 6.9$ per cent.

The mean of five determinations of the molecular weight by the freezing-point method in benzene gave 207; C₇H₁₄O₅ requires 202.

Lactone of Dimethylacetyldihydroxyglutaric Acid,

—This is obtained by boiling the lactonic acid with acetyl chloride for an hour; on cooling, the acetate crystallises out; the acetyl derivative may also be obtained by the action of acetic anhydride. It crystallises from benzene in needles, and from chloroform in plates, and melts at 136°.

0.1787 gave 0.3264 CO₂ and 0.0885
$$H_2O$$
. $C=49.8$; $H=5.5$. $C_9H_{12}O_6$ requires $C=49.98$; $H=5.6$ per cent.

The analysis was confirmed by hydrolysing with dilute sulphuric acid and titrating the acetic acid formed. On adding aniline to the acetyl-lactonic acid dissolved in benzene, the aniline salt separates at once. It melts at 121°.

—This is obtained by boiling the lactonic acid with benzoyl chloride for 4 hours; the needles, which crystallise from the solution on cooling, were dried on a porous plate and recrystallised from benzene. It melts at 209°.

0.1488 gave 0.3265
$$CO_2$$
 and 0.0666 H_2O . $C = 59.87$; $H = 4.97$. $C_{18}H_{14}O_6$ requires $C = 60.4$; $H = 5.03$ per cent.

Reduction of the Lactons of Dimethyldihydroxyglutaric Acid; aa-Dimethyl-a'-hydroxyglutaric Acid.

The lactone is easily reduced by concentrated hydriodic acid; 10 grams of the lactonic acid are dissolved in 100 grams of fuming hydriodic acid, and the mixture boiled gently with 10 grams of red

phosphorus for 8 hours. It is then neutralised with sodium carbonate, shaken with ether to remove neutral oils, acidified with hydrochloric acid, and evaporated to dryness on the water-bath after being mixed with sand; the product obtained on extracting the residue with ether, crystallises from water in large prisms melting at 152°. It appears to be the lactone of aa-dimethyl-a'-hydroxyglutaric acid,

0.1508 gave 0.2942 CO₂ and 0.0865 H₂O. C = 53.20; H = 6.3. $C_9H_{10}C_4$ requires C = 53.16; H = 6.33 per cent.

The yield of this acid represents 60 per cent. of the hydroxylactone; at the same time, an acid is obtained melting at 176°, and forming a copper salt insoluble in water.

aa-Dimethyl-a'-hydroxyglutaric acid is not reduced by sodium amalgam, or by prolonged treatment with hydriodic acid and phosphorus in a sealed tube, neither is it reduced by the action of sodium on the boiling solution of the acid in ethylic or amylic alcohols.

Methylic Salt of the Lactone of aa-Dimethyl-a'-hydroxyglutaric Acid,

$$\begin{array}{c} \text{COOCH}_8 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{C(CH}_8)_2 \\ \text{C} - - - \text{CO} \end{array}$$

—This is obtained by passing hydrogen chloride into a solution of the lactonic acid in methylic alcohol. When recrystallised from benzene, it melted at 69°.

0.2112 gave 0.4299
$$CO_2$$
 and 0.1452 H_2O . $C = 55.62$; $H = 7.6$. $C_8H_{12}O_4$ requires $C = 55.81$; $H = 7.58$ per cent.

The following homologues of the substances mentioned in this paper were also prepared for purposes of comparison, the methods of preparation being in all cases identical with those used in the preparation of the derivatives of methylic dimethylacetoacetate.

Ethylic γ -bromomethylethylacetoacetate. This boils at 164°, under a pressure of 75 mm.

0.1642 gave 0.1215 AgBr. Br = 31.5 per cent. $C_9H_{15}BrO_8$ requires Br = 31.87 per cent.

Ethylic γ -cyanomethylethylacetoacetate. This boils at 138°, under a pressure of 35 mm.

Lactone of an-methylethyl- $\beta\gamma$ -dihydroxyglutaric acid. This melts at 165° .

0.2021 gave 0.3770 CO₂ and 0.1168 H₂O. C = 50.88; H = 6.42. $C_8H_{12}O_5$ requires C = 51.07; H = 6.38 per cent.

Ethylic γ -bromodisthylac (toacetate. This boils at 164°, under a pressure of 75 mm.

0.1213 gave 0.0865 AgBr. Br = 30.36. $C_{10}H_{17}BrO_{8}$ requires Br = 30.19 per cent.

Ethylic γ -cyanodiethylacetoacetate. This boils at 158°, under a pressure of 75 mm.

Lactone of aa-diethyl-a'β-dihydroxyglutaric acid. This melts at 159°.

0.1403 gave 0.2743 CO₂ and 0.0736 H₂O. C=53.31; H=5.90. C₇H₁₄O₅ requires C=53.46; H=5.94 per cent.

In conclusion, I wish to express my thanks to Prof. W. H. Perkin, jun., for valuable advice, and to Mr. F. H. Lees for kindly undertaking most of the analyses contained in this paper.

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XLI.—Bromomethylfurfuraldehyde.

By Henry J. Horstman Fenton, M.A., and Miss Mildred Gostling, B.Sc., Bathurst Student of Newnham College.

In a previous communication (Trans., 1898, 78, 554), it was shown by the present authors that certain carbohydrates, when treated with hydrogen bromide in ethereal solution, give an intense and beautiful purple colour. It was suggested that the reaction would probably be of service in distinguishing certain typical classes of carbohydrates, and that it might be employed for the detection of these in natural products.

The examination of a considerable number of carbohydrates of various classes led to the following generalisations.

- 1.—With ketchexcess (levulose, sorbose), the purple colour appears after a few minutes, and becomes very intense in about one hour; and substances which, by hydrolysis, are capable of giving rise to these compounds (cane sugar, inulin) give a similar effect, only rather more slowly, the maximum colour being attained in about two hours.
- 2.—Hexaldoses (dextrose, galactose), and substances capable of giving rise to them (milk sugar, maltose, dextrin), show, in the first instance, various shades of yellow, brown, or red, and it is only after long standing that a purple colour is apparent. This colour, however, never approaches in brilliancy or intensity that obtained with substances mentioned in 1.

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3.—Carbohydrates whose molecules contain less than 6 atoms of carbon (arabinose, glycollic aldehyde) give brown or red colours without any appearance of purple, and the polyhydric alcohols show only a yellow colour.

A curious exception to this general behaviour is found in the case of xylose, with which a deep purple colour is obtained after a few hours; this circumstance is being further investigated.

The function of the ether in the above reaction appears to be merely that of a convenient solvent, since similar colour changes can be brought about by conducting gaseous hydrogen bromide over the dry carbohydrate. In making the experiments, it is advisable, for the sake of comparison, to employ a definite proportion of the ethereal solution and carbohydrate to be examined; in the experiments mentioned, 0.5 gram of the substance was mixed with 7.5 c.c. of a solution of hydrogen bromide in dry ether which had been saturated at about 15°, and allowed to remain in a closed vessel.

An investigation has now been undertaken with the object of throwing light upon the nature and mode of formation of this colourgiving substance, and, after some considerable difficulties, it has been isolated in a crystalline state.

If the purple ethereal solution is evaporated in a vacuum desiccator over solid potash and sulphuric acid, a purplish-black, gummy mass is obtained, and a similar result is brought about by precipitating the ethereal solution by light petroleum. On the addition of water or alkalis to the solution, the purple colour is at once discharged with separation of a dark precipitate. If, after shaking the purple mixture with excess of sodium carbonate, the ether solution is evaporated, a dark, yellowish-brown oil remains, which gives again the purple colour on the addition of hydrogen bromide. Strong hydrochloric or nitric acids give a beautiful rose colour, and strong sulphuric acid a fine but transient purple.

This oil is practically non-volatile, even under reduced pressure or in steam, and the product first obtained, which was prepared from cane sugar, obstinately refused to crystallise; later experiments however, have shown that even this product may be made to crystallise, in part, at any rate, by 'sowing' with a crystal of the substance subsequently obtained.

With landose, however, if certain precautions be taken, the product obtained in a similar way invariably crystallises when the strong ethereal solution is allowed to evaporate. In order to obtain this result, the following method is now employed.

Five hundred c.c. of a solution prepared by saturating dry ether with dry hydrogen bromide at 15° is poured on to about 100 grams

of crystallised levulose,* and the mixture is occasionally shaken and cooled if necessary, since a somewhat violent action often sets in after a few minutes. After standing for some time, generally 12 to 24 hours, the dark purple mixture is shaken with a saturated solution of sodium carbonate, in small portions at a time, and then with dry sodium carbonate until the reaction is decidedly alkaline to litmus; the ethereal solution is then decanted, and the dark brown residue repeatedly extracted with ether. The joint ether-extracts, which are deep yellow or orange, are left over calcium chloride for 12 hours or more, and the greater part of the ether is then distilled off, preferably under somewhat diminished pressure; the deep orange or brown oil thus obtained is again taken up with a small quantity of dry ether and filtered, if necessary, from a small quantity of a black insoluble substance. This solution, on being allowed to evaporate in an open dish, soon begins to deposit beautiful, orange-yellow, transparent prisms; crystallisation may be promoted, if necessary, by stirring, or by the addition of a little light petroleum. The yield of crude crystals is about 20-25 grams. The substance, which dissolves very easily in ether, chloroform, alcohol, or benzene, but with difficulty in boiling light petroleum, crystallises well from any of these solvents; light petroleum, however, affords the best means of purifying The impure crystals soon darken and decompose on keeping, so that it is advisable to purify them at once in this way. When pure, they are quite permanent.

The original orange, or deep golden-yellow, crystals behave with acids exactly in the same way as the oil above mentioned, giving intense and beautiful colours with strong hydrochloric, nitric, sulphuric, and hydrobromic acids; after one or two recrystallisations, however, they become pale yellow, and now give little, if any, colour with hydrochloric or nitric acids, and only a brown with sulphuric acid. With hydrogen bromide, however, best in ethereal solution, they give an intense purple exactly resembling the colour originally obtained; this colour appears even more quickly than in the case of ketohexoses, and becomes intense after a few minutes. The colours which the other acids give with the impure crystals are evidently due to the presence of traces of hydrogen bromide.

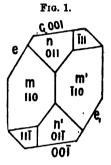
From these observations, it is evident that the substance here isolated is the cause of the purple colour obtained in the original

The first experiments were made with the pure substance, but it is now found that the 'commercial' crystallised lævulose answers perfectly well for this preparation. Ordinary methylated ether is used after it has been carefully washed and dried in the usual manner. It occasionally happened that a specimen of methylated ether was supplied, which, after careful washing, and drying over calcium chloride and even over sodium, gave an indifferent or abnormal colour. But by making use of the distillate from the subsequent operation, the results are uniformly good, even after the ether has been dried for only 24 hours over calcium chloride.

experiments. The pure crystals, which contain bromine, melt sharply at 59.5°—60.5°; heated to a higher temperature, they decompose suddenly and somewhat explosively, giving a dense, black smoke mixed with a pink or light purple sublimate, the latter being apparently due to the action of liberated hydrogen bromide on traces of the original substance which escape decomposition.

Professor Lewis has very kindly undertaken the examination of these crystals, and the authors wish to express to him their best thanks. His report is as follows.

"The crystals of bromomethylfurfuraldehyde are oblique, and belong to the holohedral (plinthoid) class." The habit of the best crystals is well given by the plan, Fig. 1, in which the plane of symmetry is in



the paper. The forms are: $c\{001\}$, $e\{201\}$, $m\{110\}$, $n\{011\}$, $o\{111\}$; and the crystal elements are: $\beta = 80^{\circ} 42'$; $a:b:c=1\cdot2427:1:1\cdot0071$.

"The following are some of the principal angles calculated and observed.

	Calculated.	Observed (mean).	
cs	52°15·6′	52°2′	
mm'	78 31	78 22	
nn'	89 2	89 5	
co	56 21.2	56 35	
cm'	95 52	95 56	
oo'	99 2	98 50	
no	31 44	31 48	
nm'	61 18	61 26	
nm	51 24	51 24	

"The crystals are very brittle, and the optic characters have not been determined. The plane of the optic axes seems to lie in the plane of symmetry, and the extinction is inclined to the vertical at an angle of 44° , and the line lies in the obtuse angle between the axes of x and z."

In cold water, the substance is practically insoluble, but it is soluble to some extent in boiling water, and dissolves in caustic alkalis with a deep orange-red colour; its solutions permanently stain the skin a deep brown. Its solution in dilute alcohol quickly reduces ammoniacal silver nitrate and Fehling's solution, and with a solution of rosaniline salt decolorised by sulphurous acid it gives, after some time, a deep purplish-red colour.

Phenylhydrazine acetate gives a buff or salmon-coloured precipitate, which, however, is very unstable; it soon turns dark-coloured, and cannot be recrystallised from any of the ordinary solvents without decomposition.

For analysis, the substance was recrystallised first from light petroleum, and afterwards from ether or chloroform, and dried in a vacuum.

L 0.1478 gave 0.2060 CO₂ and 0.0361 H₂O.

II. 0.1712 , 0.2379 CO₂ , 0.0416 H₂O.

III. 0.2380 , 0.3340 CO_2 , $0.0550 \text{ H}_2\text{O}$.

IV. 0.2478 , 0.2460 AgBr. V. 0.2915 gave 0.2935 AgBr.

If an alcoholic solution of silver nitrate is added in excess to a solution of the substance, also in alcohol, the whole of the bromine is immediately precipitated as silver bromide.

VI. Treated in this way, 0.2145 gave 0.2126 AgBr.

	Found.					
	ĭ.	II.	III.	IV.	v.	VI.
C	38.01	37 ·89	38.26			
H	2.71	2.69	2.56			
Br	• • • • • • • • • • • • • • • • • • • •			42.16	42.84	42 ·08

The simplest formula which corresponds to these numbers is $C_6H_5BrO_2$; this requires C=38.09; H=2.64; Br=42.32 per cent.

The molecular weight was determined by Raoult's method, using acetic acid (m. p. 16.9°) as solvent.

Weight of solvent.	Weight of substance.	Depression of freezing point.	Molecular weight.
18.94	0.2762	0.312	182.1
·	0.8302	0.902	189.5

Molecular weight for $C_6H_5BrO_2 = 189$.

From this formula, and from certain properties of the substance, such as the yellow colour and the power of staining the skin, it was at first thought possible that it might be a quinone derivative, $C_6H_4O_2$, HBr, or, from the formula, it might be a substituted dihydroxybenzene, $C_6H_8Br(OH)_2$; but by no process of reduction or oxidation, &c., could any recognisable benzenoid compound be obtained from it.

An alternative, however, is that the substance may be a bromoderivative of methylfurfuraldehyde, C₆H₆O₂. This supposition ap-

peared probable from some of the reactions of the substance; with aniline acetate paper, for example, its solutions give at first only a pale yellow colour, but this, after some time, becomes changed to a bright orange, the behaviour in this respect entirely resembling that of methylfurfuraldehyde itself (Hill and Jennings, Amer. Chem. Journ., 1893, 15, 162).

Moreover, it has been shown by Düll (Chem. Zeit., 1895, 19, 216) that, by heating inulin with oxalic acid solution under pressure, a derivative of methylfurfuraldehyde is produced; this substance was afterwards further examined by Kiermayer (loc. oit., 1003), who prepared it in a similar way from cane sugar, the dextrose being apparently unacted on. It is described as a colourless syrup which rapidly turns yellow on exposure to the air; it is soluble in water, alcohol, and ethylic acetate, and gives a colour reaction with aniline acetate similar to that produced by furfuraldehyde. It also gives colour reactions with thymol and with phloroglucinol. It cannot be distilled unchanged. On oxidation with ammoniacal silver nitrate, it yields a hydroxymethylpyromucic acid melting at 148°. The hydrazone and the two oximes (anti and syn) are crystalline. The substance is considered to be β -hydroxy- δ -methylfurfuraldehyde,

produced from levulose by loss of $3H_2O$, $C_6H_{12}O_6 - 3H_2O = C_6H_6O_8$. Its formation is explained by supposing that the two terminal $CH_2 \cdot OH$ groups of levulose lose a molecule of water, one becoming oxidised and the other reduced, so that a methyl and an aldehyde group result.

The position of the hydroxyl group is uncertain, but on various grounds it is considered to occupy the β -position. In explanation of the formation of a furfuran nucleus, reference is made to Tollens' lacton' formula for lævulose, so that, upon this view, the relation might perhaps be indicated in some such way as the following.

On the supposition just mentioned, it would therefore follow that there should be a close relation between the new bromo-derivative and the compound discovered by Düll. It was mentioned that the bromine in the former compound is entirely precipitated by silver nitrate, and the solution might then contain a substance identical or isomeric with Düll's compound. Oxidation with silver oxide should yield one of the hydroxymethylpyromucic acids, and perhaps, by careful oxidation with other agents, it should be possible to obtain one of the bromomethylpyromucic acids.

Oxidation with Silver Oxide.—Following the method employed by Hill and Jennings in the oxidation of methylfurfuraldehyde (loc. cit., 167), the substance was mixed with a considerable excess of freshly precipitated silver oxide suspended in water and heated to boiling for 20 minutes; sodium carbonate was then added to precipitate the silver in solution, the mixture was again boiled, filtered, evaporated to small bulk, again filtered, acidified with hydrochloric acid, and, as no acid separated on cooling, extracted with ether. The ethereal solution, on evaporation, left a brownish residue which, when recrystallised from ethylic acetate with the addition of a little animal charcoal, gave a white, crystalline mass; better crystals were obtained, however, by using a mixture of absolute alcohol and toluene. Under the microscope, the lustrous, crystalline mass was seen to consist of long, transparent prisms or plates. The acid was fairly easily soluble in water, alcohol, and hot ethylic acetate, but only very sparingly in boiling chloroform. It melted and decomposed at 162-163°. dried in a vacuum and analysed, with the following result.

0.1264 gave 0.2334 CO₂ and 0.0495 H₂O. C = 50.35; H = 4.35. $C_6H_6O_4$ requires C = 50.70; H = 4.23 per cent.

The melting point and properties of this acid entirely agree with the shydroxymethylpyromucic acid obtained by Hill and Jennings by the action of water on the corresponding bromo-acid (loc. cit., 181), and the acid is different, therefore, from that obtained by Kiermayer from Düll's compound.

The constitution of the former acid may be taken as well established. That the methyl group occupies the δ -position follows from Maquenne's formation of methylfurfuraldehyde from rhamnose, and the constitution of the latter as determined by Fischer and Tafel; moreover, the position of the hydroxyl group in the side chain is concluded from the 'reactive' properties of the bromo-acid from which it is derived, properties which are in striking contrast with those of the isomeric β -acid.

For these reasons, there can be but little doubt that the substance at present under discussion is ω-bromo-δ-methylfurfuraldehyde,

Its formation may be expressed by the relation $C_6H_{12}O_6 + HBr - 4H_2O = C_6H_5BrO_2$, and it is evident that, in representing the formation VOL. LXXV.

of the terminal groups an explanation must be offered which is somewhat different from that which accounts for the production of Dull's compound.

Action of Silver Nitrate.—It has been already stated that the bromine in the original substance is quantitatively separated by precipitation with silver nitrate in alcoholic solution; in order to examine the nature of this solution, a weighed quantity of the substance was dissolved in dilute (50 per cent.) alcohol, and mixed with slightly more than the calculated amount of silver nitrate dissolved in the same solvent. After filtration, the liquid was treated with a few drops of barium chloride solution to remove excess of silver, and, being strongly acid, it was then shaken with excess of barium carbonate and again filtered. After being kept in a vacuum desiccator for a day or two, yellow drops began to separate, and collected as a heavy oil at the bottom of the vessel. When most of the supernatant liquid had evaporated, the residue was taken up with absolute alcohol, filtered from barium salts, and the alcohol again evaporated. The oil or syrup thus obtained was moderately soluble in cold water. and dissolved easily in alcohol or ether; the solutions readily reduce Fehling's solution and ammoniacal silver nitrate, and with aniline acetate paper give a bright orange to brick-red coloration. With thymol and a few drops of moderately strong sulphuric acid, a fine pink colour is obtained, and phloroglucinol, with acids, gives an intense brownish-red. An ethereal solution of hydrogen bromide gives, immediately, an intense purple colour.

On heating, the oil begins to show signs of boiling at about 80°. but the temperature continues to rise, and no fixed boiling point is indicated. A small quantity of liquid distils over at about 200°, and behaves generally like the unaltered substance.

If the aqueous solution is treated with the calculated quantity (1 mol.) of phenylhydrazine as acetate, the liquid at once turns milky, and a red oil slowly separates, but this shows no signs of solidification. even after being kept for some days in a vacuum desiccator, or after purification by dissolving in hot dilute alcohol, from which it separates on cooling.

On oxidising this substance with silver oxide in the manner already described, an acid is obtained which melts at 162-163°, and is evidently identical with that obtained from the original substance.

From these observations, it is evident that this product bears a close resemblance to Düll's hydroxymethylfurfuraldehyde, but differs from it in some important particulars-for example, in the formation of a liquid hydrazone, and the character of the hydroxymethylpyromucic acid obtained from it on oxidation.

Action of Water.—A solution of the substance in dilute alcohol is

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neutral to litmus, but on boiling it with water it slowly dissolves and the solution becomes strongly acid. If it is boiled with water, and excess of barium carbonate added to the hot solution, the filtered liquid, on extraction with ether, gives a product which appears to be identical in every way with that obtained by the action of alcoholic silver nitrate.

It appears, therefore, that the substance very readily undergoes hydrolysis, giving hydrogen bromide and hydroxymethylfurfuraldehyde. This fact, and the ease with which the original substance reacts with silver nitrate, further support the view, expressed above, that the bromine occupies a position in the side chain rather than in the nucleus.

Action of Sulphurous Acid.—When powdered crystals of the purified substance are covered with water, and sulphur dioxide is passed into the mixture, the gas is rapidly absorbed for a considerable time, and on allowing the mixture to remain for some hours, with further saturation by the gas if necessary, the whole of the solid dissolves; this solution, when treated with excess of caustic alkali, gives a magnificent blue or plum colour. Ether, chloroform, or benzene extract this colour-giving substance from the solution, and leave it as a crystalline solid on evaporation.

For the isolation of this substance, the mixture, after saturation with sulphur dioxide, was allowed to stand for 24 hours or more, and then neutralised with barium carbonate. (For convenience, it is advisable, before neutralising, to remove the excess of sulphur dioxide and part of the liquid by distillation under reduced pressure). It is then extracted 5 or 6 times, or more, with one of the abovementioned solvents, the solution dried over calcium chloride, and the solvent distilled off, when a yellow or orange oil is left which generally sets to a crystalline mass on cooling, but sometimes remains in a superfused condition, and requires shaking, or the addition of a few drops of water, to promote crystallisation. It is then recrystallised from the smallest possible quantity of boiling water, from which it separates on cooling as a bulky yellow or orange, crystalline precipitate; under the microscope, this is seen to consist of long, transparent needles. After again crystallising from hot water or hot dilute alcohol, with the addition, if necessary, of animal charcoal, the colour is very pale golden-yellow. It is easily soluble in cold acetone, chloroform, glacial acetic acid, or hot alcohol or benzene. and dissolves sparingly in cold alcohol or ether, or hot water. It melts sharply at 116.5-117.5°, and when heated to a higher temperature, a considerable portion vaporises unchanged and condenses as a crystalline sublimate. It is also slightly volatile with steam. Its alcoholic or aqueous solutions give, with caustic potash or soda, a

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magnificent blue colour, which in deep layers 'appears red or plum-coloured; this colour soon fades on standing. With hydrogen bromide in ether, it gives an intense but transient purple colour.

With aniline acetate, solutions of this product give immediately a beautiful, bright green colour; a mixture of aniline with the substance in alcoholic solution gives no colour, but on the addition of acetic, tartaric, or other organic acid, the green colour appears at once. Mineral acids appear only to produce a similar effect in certain states of dilution.

The substance, crystallised from hot water and dried at 100°, was analysed.

I. 0.1268 gave 0.2991 CO₂ and 0.0455 H₂O. C = 64.33; H = 3.98.

This result appeared to be anomalous, since it could not be reconciled to any C_s-formula, or multiple thereof, consequently several more analyses were made with specimens which were variously treated. The melting point, however, continued to be quite constant, and the results of analysis practically the same.

- II. Recrystallised from hot water and then from hot alcohol and dried in a vacuum. M. p. 116.5—117°.
- III. Recrystallised from hot water containing sulphur dioxide. Dried in a vacuum. M. p. 117°.
- IV. Recrystallised from hot water and then from hot alcohol, both containing sulphur dioxide. Dried at 100°. M. p. 117.5°.
 - II. Found, C = 64.50; H = 4.00 per cent.
 - III. , C = 64.48; H = 3.98 ,, IV. , C = 64.47; H = 3.83 ,,

The simplest formula which can satisfactorily explain these numbers appears to be $C_{11}H_8O_4$, which requires C=64.70; H=3.92 per cent.

The molecular weight was determined by Raoult's method, with acetic acid as solvent.

Weight of solvent.	Weight of substance.	Depression of freezing point.	Molecular weight.
I. 9·92	0.2760	0.504	215.2
II. —	0.4203	0.774	$213 \cdot 4$
III. 15·57	0.1461	0.169	216.5
IV. —	0.3756	0.436	215.7

It must, therefore, be concluded that the formula is $C_{11}H_8O_4$, the molecular weight of which is 204.

The substance is a powerful reducing agent and acts decidedly, though feebly, as a photographic developer; it also reacts with phenylhydrazine, but does not give the aldehydic reaction with Schiff's reagent. It would be easy, of course, to make assumptions

as to its constitution; it might, for example, be methylfuril, $C_4H_3O \cdot CO \cdot CO \cdot C_4H_3O \cdot CH_3$, but this is a mere conjecture, and the authors prefer to reserve the discussion of its nature and mode of formation, for a future communication, when further experiments are completed.

Oxidation with Chromic Acid.—If the original bromo-derivative is finely powdered, covered with dilute sulphuric, acid, and a solution of chromic acid is slowly added to the mixture, a violent action takes place with considerable rise of temperature. By using only 1 atomic proportion of oxygen and keeping the mixture cool, a crystalline acid was obtained which closely resembled the \(\omega\)-bromomethylpyromucic acid of Hill and Jennings. Its solutions gave no precipitate with silver nitrate in the cold, but after boiling the aqueous solution there was copious precipitation of silver bromide. The quantity of the acid obtained, however, was very small, the greater part of the substance remaining unchanged, so that it has not yet been fully examined. But if excess (5 atoms) of oxygen is added, and the temperature allowed to rise, another crystalline acid is obtained which is very sparingly soluble in water, and sublimes on heating.

These acids, together with several other interesting derivatives of the aldehyde, are being investigated.

The authors wish gratefully to acknowledge their indebtedness to the Government Grant Committee of the Royal Society, for the funds which have enabled them to carry out this investigation.

XLII.—A Reaction of some Phenolic Colouring Matters.

By ARTHUR GEORGE PERKIN, F.R.S.E.

During the examination of certain hydroxyanthraquinone derivatives, it was observed that alcoholic solutions of their salts are completely decolorised only with difficulty by acetic acid, and this suggested the presence of some stable salt. On reversing the experiment, this was found to be the case, for alcoholic solutions of these colouring matters decompose potassium acetate, forming sparingly soluble, crystalline salts in which one hydrogen only had been replaced by the metal. As quercetin possessed a similar property, it was desirable to determine if this reaction was in any way general, and to assign, if possible, a reason for the marked acidity of these colouring matters. Salts of certain yellow colouring matters have already been described, which, at first sight, are analogous to those formed by the above method.

Examination, however, shows that, in the majority of cases, these have no value, for their percentage composition, calculated from the older formulæ assigned to them, will not agree with that required for any salt of the colouring matter having the correct molecular weight; a description of these is given in the experimental portion of this paper. Of the numerous colouring matters here studied, some few were obtained by purchase from Merck of Darmstadt, or prepared synthetically. The majority I have either isolated from their natural sources, or from the commercial preparations which are employed in this department.

The Alizarin Group.

Alizarin, as is well known, forms potassium, barium, calcium, and other derivatives in which two atoms of hydrogen are replaced by the metal, but no acid salts of this colouring matter have been hitherto described; the addition of alcoholic potassium acetate to a solution of alizarin in boiling absolute alcohol causes the separation of a crystalline precipitate, and this may be collected and washed with alcohol, in which it is but sparingly soluble.

0.9495, dried at 160°,* gave 0.2935 K_2SO_4 . K = 13.86. $C_{14}H_7O_4K$ requires K = 14.02 per cent.

Monopotassium alizarin forms a glistening mass of violet-coloured needles, almost insoluble in cold water, a property distinguishing it from the soluble dipotassium salt, which it considerably resembles in appearance. That it could not be a compound of alizarin with potassium acetate analogous to that yielded by hesperitin (Trans., 1898, 73, 1035) was readily ascertained by a study of its decomposition with hydrochloric acid.

0.9453 gave 0.8190 $C_{14}H_8O_4$. Found, 86.62. $C_{14}H_7O_4K$ requires $C_{14}H_8O_4 = 86.33$ per cent.

If it is suspended in cold water and the mixture heated to boiling, little is dissolved until the temperature is within a few degrees of boiling, when a violet solution is produced, which is redder in tint than that of the dipotassium salt. In this way, no apparent decomposition of the salt ensues, which, as will later appear, is characteristic only of this group. Alizarin remains almost unaffected on digestion with aqueous potassium acetate, and even in sealed tubes at 160° it is but imperceptibly tinged violet. As the presence of water is inimical to the formation of this and the following salts, absolute alcohol has been employed in every case, for not only is the yield

* Although the employment of absolute alcohol should preclude the presence of water of crystallisation in these salts, in each case in this paper, to avoid mistake, they have been dried at this temperature before analysis.

thereby increased, but the separation of the salt is certain, which is not the case if a more dilute alcohol be employed.

Monosodium alizarin, C₁₄H₇O₄Na, is identical in appearance and general properties with the potassium salt. A solution of sodium acetate in dilute alcohol was added to that of the colouring matter in absolute alcohol, and to remove any precipitated acetate from the salt produced, this was rinsed with a little water and finally washed with alcohol.

 $\begin{array}{lll} 0.8725 \ \ \text{gave} \ \ 0.2250 \ \ \text{Na}_2 \text{SO}_4. & \text{Na} = 8.35. \\ 0.7750 & \text{,,} & 0.1920 \ \ \text{Na}_2 \text{SO}_4. & \text{Na} = 8.24. \\ & & \text{Theory requires Na} = 8.77 \ \ \text{per cent.} \end{array}$

In like manner, alizarin decomposes ammonium acetate, forming an ammonium salt which crystallises in violet needles; this, probably, has the formula $C_{14}H_7O_4\cdot NH_4$, but was not analysed, as on gentle heating it is converted into alizarin, with evolution of ammonia.

Monobarium alizarin, $(C_{14}H_7O_4)_2Ba$, is formed on adding barium chloride to a boiling aqueous solution of the monopotassium or sodium salts. The precipitate at first produced is violet-coloured, but gradually assumes a duli red tint. Found, $Ba=22\cdot19$. Theory, $Ba=22\cdot32$ per cent.

It forms a glistening mass of salmon-red needles, sparingly soluble in boiling water, with a red-violet coloration. Heated to 160°, it becomes of a violet hue, which is permanent on cooling, and it would thus appear that this salt exists in two modifications.

Monocalcium alizarin, $(C_{14}H_7O_4)_2Ca$, prepared in an analogous manner, is a violet-coloured, crystalline powder. Curiously enough, this was not obtained in the red condition. Found, Ca = 7.42. Theory, Ca = 7.72 per cent.

The boiling aqueous solutions of both barium and calcium salts dye mordanted calico.

Monopotassium anthragallol, $C_{14}H_7O_5K$.—Like alizarin, anthragallol decomposes potassium, sodium, and ammonium acetates. The above salt forms glistening, almost black needles, nearly insoluble in cold water or alcohol, soluble in boiling water, with a deep brown coloration. Found, $K=13\cdot27$. Theory, $K=13\cdot26$ per cent.

Monosodium anthragallol, $C_{14}H_7O_5Na$, closely resembles the potassium salt. Found, Na=8.23. Theory, Na=8.27 per cent.

Monobarium anthragallol, $(C_{14}H_7O_5)_2$ Ba, obtained from the above salts by double decomposition, is a black, amorphous powder, which dissolves sparingly in boiling water with a brown coloration. Found, Ba = 21·10. Theory, Ba = 21·22 per cent.

Monopotassium purpurin, $C_{14}H_7O_5K$, forms a glistening mass of red needles somewhat more readily soluble in alcohol and water than the

corresponding derivative of alizarin and anthragallol; these solutions are red. Found, K = 13.54. Theory, K = 13.26 per cent.

The sodium derivative, $C_{14}H_7O_5Na$, is similar in appearance. Found, Na=8.30. Theory, Na=8.27 per cent.

The barium and calcium salts are amorphous.

Further experiments indicated that all other members of the alizarin group of colouring matters which contain two hydroxyls in the ortho-position relatively to one another react with potassium acetate, yielding monopotassium derivatives. It appeared unnecessary to critically examine these, for not only would much time be required for their purification in quantity, but as the salts of the tetra-, penta-, and hexa-hydroxyanthraquinones are not insoluble in alcohol in those instances examined, they would be more difficult to obtain in a pure condition. Of the substituted alizarins, β -nitroalizarin and monobromalizarin react readily; the potassium derivative of the latter gave K = 10.39. Theory requires 10.92 per cent.

A boiling alcoholic solution of metahydroxyanthraquinons becomes red on the addition of potassium acetate; the liquid, on evaporation, left a pasty mass of crystals, which was drained and washed with alcohol. The product was yellow, gave $K=2\cdot17$ on analysis, and consisted evidently of unchanged metahydroxyanthraquinone contaminated with a trace of its potassium salt, for it dissolved in boiling alcohol with a red colour. Quinizarin and alizarin methyl ether $[OH:OCH_8=1:2]$ do not decompose potassium acetate in this manner.

The Flavone Group.

Under this heading, the behaviour of myricetin, quercetin and its ethers, morin, fisetin, luteolin, apigenin, and chrysin towards the alkali acetates will be described; recent work has indicated that all belong, or are closely allied, to this group of yellow colouring matters

Morin, $C_{15}H_5O_2(OH)_5$ (Trans., 1896, 69, 792).—A boiling alcoholic solution of this substance, on treatment with potassium acetate, readily deposits an orange-yellow, crystalline precipitate; this was washed with alcohol and dried at 160°. Found, K = 11.60. $C_{15}H_9O_7K$ requires K = 11.47 per cent.

Monopotassium morin forms glistening needles insoluble in cold water and alcohol. To confirm its composition, it was decomposed with acid, and the morin collected and weighed.

1.0737 gave 0.9525 $C_{15}H_{10}O_7$. Found, 88.71. $C_{15}H_{0}O_7K$ requires $C_{15}H_{10}O_7 = 88.82$ per cent.

It is somewhat readily soluble in boiling water, forming an orangeyellow solution which, on cooling, deposits a finely-divided, crystalline precipitate; this, however, was found to consist chiefly of morin, together with a small quantity of the unaltered potassium salt. On neutralising the yellow filtrate, a further quantity of morin separated. The decomposition of the salt with boiling water probably occurs as follows,

$$5C_{15}H_{10}O_7K = 4C_{15}H_{10}O_7 + C_{15}H_5O_7K_5$$

morin being liberated, and a portion then converted into the saturated alkali salt by the potassium hydroxide simultaneously produced.

Monosodium morin, $C_{15}H_9O_7Na$, closely resembles the potassium salt. Found, Na = 6.87. Theory requires Na = 7.09 per cent.

Magnesium morin, $(C_{15}H_9O_7)_2Mg$, obtained by the action of magnesium acetate on alcoholic morin solution, forms orange-yellow needles. Found, Mg = 3.52. Theory requires Mg = 3.88 per cent.

Barium morin, $(C_{15}H_9O_7)_2$ Ba, is deposited as a glistening, orange-coloured, crystalline powder when barium chloride is added to a freshly prepared solution of the above potassium salt in boiling water. It is collected while hot, and washed first with a little boiling water and then with alcohol. Found, Ba = 18.45. Theory requires Ba = 18.58 per cent.

Hlasiwetz and Pfaundler (Jahresbericht, 1864, 557) have described the following metallic derivatives of morin, $C_{12}H_9O_6K$, $(C_{12}H_9O_6)_2Ca$, $(C_{12}H_9O_6)_2Zn$, the former being obtained by the action of hot, aqueous potassium carbonate solution on the colouring matter; as, however, the formula of morin (Trans., 1896, 69, 792) is $C_{15}H_{10}O_7$, the compounds just mentioned cannot exist. As will be seen below, the salt $C_{15}H_9O_7K$ (K=11.47 per cent.) is readily prepared by means of potassium carbonate in presence of alcohol, so that the compound of Hlasiwetz and Pfaundler (K=13.54 per cent.) may possibly be a very impure form of that above described.

Monopotassium tetrabromomorin, $C_{15}H_5Br_4O_7K$, is obtained by cautiously adding potassium acetate to the boiling alcoholic solution of the tetrabromo-compound; the product is washed first with alcohol, and then with water to remove a more soluble salt, and finally with alcohol. It forms minute, yellow needles. Found K=5.97 and 6.29. Theory requires K=5.94 per cent.

Dipotassium Tetrabromomorin, $C_{15}H_4Br_4O_7K_2$.—When excess of potassium acetate is employed in the above reaction, the mono-derivative is not obtained, a bright orange-coloured, gelatinous precipitate separating which is readily soluble in cold water; this should be rapidly collected and washed with alcohol, otherwise a darkening frequently ensues, the result of some decomposition. Found, $K=11\cdot25$. Theory requires $K=11\cdot24$ per cent.

It is a bright orange-coloured powder, an aqueous solution of which

gives a precipitate with barium chloride; examination of a somewhat discoloured sample showed that this decomposition probably has for a result a slight loss of bromine. It was digested with boiling glacial acetic acid, and the nearly colourless, crystalline product separated from the yellow mother liquor by filtration, and washed with alcohol. On analysis, this gave C = 32.59, H = 1.49, whereas tetrabromomorin requires C = 29.12, H = 0.97 per cent.

Morin tetramethyl ether (loc. cit.) does not decompose alcoholic potassium acetate solution.

Quercetin, C15H5O0(OH)5, behaves towards potassium acetate in a similar manner to morin.

Monopotassium quercetin, C₁₅H₀O₇K. Found, K=11.43. Theory requires K=11.47 per cent. This is an orange-yellow, crystalline powder consisting of small needles, is almost insoluble in cold water and alcohol. On decomposition with acid, 88.54 per cent. of quercetin was obtained, theory requiring 88.82 per cent. Boiling water dissolves it, forming an orange-yellow solution which, on cooling, deposits a flocculent, yellow precipitate, consisting of quercetin contaminated with a trace of the unattacked salt. The filtrate was yellow, and yielded quercetin on neutralisation, and it was evident that monopotassium quercetin is decomposed by boiling water in an analogous manner to the corresponding morin compound.

Monosodium quercetin, C15H2O7Na, closely resembles the potassium salt. Found, Na = 7.07. Theory requires Na = 7.09 per cent.

Hlasiwetz and Pfaundler have described (Jahresbericht, 1864, 560) salts of quercetin of the formulæ $K_2C_{24}H_{16}O_{11}$ (K=13.98 per cent.), $Na_2C_{24}H_{16}O_{11}$ (Na = 8.74 per cent.), and $Zn_1C_{24}H_{16}O_{11}_1Zn(OH)_2$; the molecular weight of quercetin is represented by C15H10O7, so that the formulæ of these compounds are not only erroneous, but their percentage composition indicates that they are mixtures.

Quercetin does not appear to decompose ammonium and magnesium acetates, as is the case with morin, and attempts to produce a barium salt from the potassium salt by double decomposition gave unsatisfactory results; the product in the latter case does not separate at the boiling temperature, and although, on cooling, crystals of the salt (C₁₅H₂O₇)₂Ba were evidently present, they were contaminated with a gelatinous product containing a higher content of barium, and this This analysis gave Ba = 25.3; 24.3, whereas could not be removed. theory requires Ba = 18.51 per cent.

Monopotassium dibromoquercetin, C15H7Br2O7K, is a semi-crystalline, yellow powder which, on long digestion with alcoholic potassium acetate, acquires a green tint. Found, K = 7.68. Theory requires K = 7.83 per cent.

Rhamnetin (quercetin monomethyl ether), C₁₅H₅O₂(OCH₃)(OH)₄,

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dissolved in boiling alcohol, gives no precipitate with potassium acetate, although the liquid acquires an orange-yellow tint; this is evidently due to the presence of the large quantity of alcohol required for the solution of the rhamnetin, as, on evaporation to a small bulk, minute, orange-coloured needles separate. The salt was collected while hot and washed with alcohol.

It appears, therefore, to consist of a monopotassium derivative of a double molecule of rhamnetin. The above analyses represent distinct preparations, and the product under the microscope appeared homogeneous, for the insoluble nature of rhamnetin suggested as possible its separation with the salt in the process described. That this composition is correct, however, appears most probable, for both its glucoside, xanthorhamnin, and rhamnazin, its methyl ether (Trans., 1897, 71, 818), gave a like result (see below).

Rhamnazin, $C_{15}H_5O_2(OCH_8)_2(OH)_8$ (quercetin dimethyl ether), yields, in a similar manner, a salt crystallising in yellow needles.

Quercetin tetramethyl ether does not react with potassium acetate.

Glucosides of Quercetin.

Quercitrin.—An alcoholic solution of this substance gives no precipitate with potassium acetate, but a yellow liquid is obtained which, on evaporation, does not deposit the unchanged substance. On dilution with water, no precipitate is formed, but on long standing quercitrin slowly separates.

According to Liebermann and Hamburger (Ber., 1879, 12, 1179), the salt $C_{36}H_{36}O_{20}K_2$ separates when alcoholic potash is added to a solution of quercitrin in alcohol. The researches of Herzig (Monatch., 1885, 6, 863) show, however, that the formula of quercitrin is $C_{21}H_{22}O_{12}$, and the percentage composition of the above compound $(C_{36}H_{36}O_{20}K_2 = K 9.07 \text{ per cent.})$ does not coincide with that required for a salt derived from a compound of this molecular weight $(C_{21}H_{22}O_{12}K = K 7.73 \text{ per cent.})$.

Rutin, $C_{27}H_{82}O_{16}$ (Schunck, Trans., 1888, 53, 264) is a glucoside of quercetin which, on decomposition with acid, yields quercetin and two molecules of rhamnose, $C_{27}H_{82}O_{16} + 3H_2O = C_{15}H_{10}O_7 + 2C_6H_{14}O_6$.

hot alcoholic solution of this substance, on treatment with alcoholic potassium acetate, deposits a yellow, amorphous precipitate which increases in quantity on cooling. With this and the following glucosides, boiling solutions should not be employed, otherwise the precipitate congeals, with formation of resinous lumps which are manipulated with difficulty. The precipitate is collected, washed with alcohol, allowed to drain on a porous tile over sulphuric acid, and dried at 160° . Found, K = 6.29. $C_{27}H_{31}O_{16}K$ requires K = 6.00 per cent.

Monopotassium rutin, C₂₇H₃₁O₁₆K, is a bright yellow, hygroscopic powder, somewhat soluble in cold alcohol, readily in cold water. By the action of boiling water, it is decomposed, with regeneration of rutin, which crystallises out on cooling the solution, and a similar result also takes place in the cold, although somewhat slowly.

Violaqueroitrin (Mandelin, Jahresber., 1883, 1369,) was prepared from the flowers of Viola tricolor variensis. According to Mandelin's results, it would appear to have the formula $C_{27}H_{26}O_{15}$ (Trans., 1897, 71, 1134), calculated on the correct molecular weight of quercetin. In alcoholic solution, it behaved with potassium acetate similarly to rutin. Found, K = 6.21. $C_{27}H_{26}O_{15}K = 6.21$ per cent.

Monopotassium violaquercitrin is a yellow powder soluble in cold and decomposed by boiling water, free violaquercitrin separating on cooling. I am at present investigating this glucoside, in order to determine its identity or otherwise with osyritrin (Trans., 1897, 71, 1133), which occurs in Cape sumach.

Myrticolorin, $C_{27}H_{28}O_{16}$ (Smith, Trans., 1898, 78, 697), is the quercetin glucoside present in the leaves of Eucalyptus macrorhyncha. For the sample examined, I am indebted to the kindness of Mr. Smith. This behaves similarly to the above glucosides. The amorphous monopotassium myrticolorin, $C_{27}H_{27}O_{16}K$, is a yellow powder, closely resembling the compounds just described. Found, K=6.55. $C_{27}H_{27}O_{16}K$ requires K=6.03 per cent.

Osyritrin gives an analogous result with potassium acetate. The product was not analysed.

Xanthorhamnin, the glucoside of rhamnetin, occurs in Persian berries, from Rhamnus tinctoria. Liebermann, and Hörmann assigned to it the formula $C_{48}H_{66}O_{29}$, rhamnetin being then considered as $C_{12}H_{10}O_5$. In the light of the true formula for rhamnetin, $C_{16}H_{12}O_7$, which Herzig (Monatsh., 1888, 9, 548—561) has shown to be a quercetin monomethyl ether, xanthorhamnin, if its constitution is analogous to that of the quercetin glucosides, may be approximately represented as $C_{28}H_{86}O_{17}$, and its decomposition into rhamnetin and rhamnose as follows,

$$\mathbf{C_{28}H_{86}O_{17}+2H_2O=C_{16}H_{12}O_7+2C_6H_{14}O_6}.$$

In continuation of previous work (Trans., 1895, 67, 496), a specimen

of this substance was prepared, but its examination was postponed on account of the then somewhat recent work of Herzig (loc. cit.) in this direction. It readily reacts with potassium acetate in alcoholic solution, forming an orange-yellow, amorphous salt readily soluble in cold water, and somewhat soluble in alcohol. Found, K=3.72; 3.69. $(C_{28}H_{35}O_{17})(C_{28}H_{35}O_{17})K$ requires K=3.46 per cent.

As in the case of the rhamnetin salt, the analysis of this compound indicates a double molecule of xanthorhamnin with one hydrogen replaced by potassium. From rhamnazin, also, a similar result has been obtained, and it thus appears evident that the salts of these two colouring matters must be regarded as true compounds and not as mixtures.

Fisetin, C15H6O2(OH)4.

Monopotassium fisstin, $C_{15}H_9O_6K$, separates in the form of slender yellow needles when its boiling alcoholic solution is treated with an excess of potassium acetate. It is somewhat soluble in alcohol, and much loss is thus occasioned in the washing operations. Found, $K=12\cdot49$. Theory requires $K=12\cdot03$ per cent. Digested with boiling water, it is decomposed in a manner analogous to the salts of morin and quercetin.

Schmid (Ber., 1886, 19, 1739) has described a salt of fisetin, $C_{23}H_{14}O_9Na_2$, obtained by means of aqueous sodium carbonate solution. As this substance does not agree in percentage composition (Na = 9.58) with that required for a salt of fisetin calculated according to the true formula $C_{15}H_{10}O_6$, ($C_{15}H_9O_6Na$ requires Na = 7.46), it cannot have been a pure product.

Monopotassium myricetin, C₁₆H₉O₈K, forms orange-coloured needles which darken on oxidation, and must be rapidly collected.*

Luteolin, C₁₅H₆O₂(OH)₄, when treated as above with potassium acetate, gives a gelatinous product which would appear to consist of the monopotassium salt; on account of its soluble nature, it could not, however, be isolated in a pure condition.

From apigenin, C₁₅H₇O₂(OH)₈ (Trans., 1897, 71, 805), and chrysin, C₁₅H₃O₂(OH)₂, no insoluble salts could be obtained by this reaction; the addition of the acetate to their alcoholic solutions, indeed, produced a yellow coloration indicating the production of soluble salts, but as water precipitated the colouring matter unchanged, the compounds formed must be of an unstable nature.

An investigation of the yellow colouring matter contained in the flowers of the cotton plant (Gossypium herbaceum) has shown that this, which is probably a member of the flavone group, forms com-

[•] The somewhat peculiar properties of this salt will be described later, in connection with a further examination of myricetin now in progress.

pounds with mineral acids, and also metallic derivatives allied in character with those described above.

Xanthone Group.

Eucanthone, $C_{13}H_6O_2(OH)_2$, and gentisin, $C_{18}H_5O_2(OH)_2(OCH_8)$, were obtained from Merck of Darmstadt. No salts could be obtained from these by means of potassium acetate, and apparently no action occurred, for the unchanged substances were deposited from the solutions on cooling.

It was not possible to obtain for examination a colouring matter of this group containing two hydroxyls in the ortho-position relatively to one another, although it was interesting to examine the properties of galloflavin, a possible member in this respect.

Galloflavin, $C_{13}H_6O_9$, has been studied by Graebe and Bohn (Ber., 1887, 20, 1329), and they describe a potassium derivative, $C_{13}H_4O_9K_9$, which is obtained as the product of the oxidation with air of potassium gallate dissolved in dilute alcohol.

The purification of commercial galloflavin by crystallisation is difficult, owing to its sparing solubility, and it was, therefore, acetylated. When the colourless crystalline product thus obtained, identical with that prepared by Graebe and Bohn, is digested with boiling potassium acetate solution, it slowly dissolves, forming an orange-coloured liquid, which, on continued heating, soon deposits an orange-coloured, crystalline precipitate. This was collected and washed with alcohol. Found, K = 20.32. $C_{18}H_4O_0K_8$ requires K = 20.41 per cent.

Treated with boiling water, it is readily decomposed, with separation of galloflavin, and was identified as the salt described by Bohn and Graebe (loc. cit.).

Ketone Group.

Maclurin (pentahydroxybenzophenone), $C_{13}H_5O(OH)_5$, a colouring matter of old fustic, Morus tinctoria, was procured from Merck of Darmstadt. Its alcoholic solution is at once tinged orange-yellow by potassium acetate, but only on evaporation does a salt separate. This, which was of a gelatinous nature, was too soluble to admit of purification.

Alizarin yellow A (trihydroxybenzophenone), $C_{18}H_7O(OH)_8$ [(OH)₈ = 1:2:3], readily yields a potassium derivative, which, if the solution is concentrated, separates in minute, yellow needles somewhat soluble in alcohol. Found, $K = 15\cdot12$. $C_{18}H_9O_4K$ requires $K = 14\cdot55$ per cent.

It is decomposed by boiling water, crystals of the regenerated ketone separating.

According to Richter (J. pr. Chem., 1883, [ii], 28, 285), the dihydroxybenzophenone, obtained by the action of fused alkali on diphenylene ketone oxide, yields, with alcoholic potash, the salt $C_{12}H_9O_2K$.

Experiments with gallacetophenone (trihydroxyacetophenone) indicate that this colouring matter forms a colourless compound when treated with alcoholic potassium acetate. As the analyses of this product have not been concordant, its description is reserved for a later communication.

Colouring Matters of Unknown Constitution.

From hamatein, $C_{16}H_{12}O_6$, the colouring matter of logwood (Hamatoxylon campechianum), the monopotassium derivative, $C_{16}H_{11}O_6K$, is deposited in black granules or nodules on adding potassium acetate to its alcoholic solution; it is sparingly soluble in alcohol with a red coloration, and somewhat readily in water with a more violet tint. Found, K = 11.74. Theory requires K = 11.54 per cent.

Monosodium hæmatein, $C_{16}H_{11}O_6Na$, has similar properties. Found, Na = 7.38. Theory requires Na = 7.14 per cent.

Brazilein, the colouring matter of brazil wood, behaves similarly, but the products of the reaction could not be isolated, owing to their ready solubility in alcohol.

Santalin, $C_{15}H_{14}O_5$ (Weyermann and Haffely, Annalen, 1850, 74, 226), a red colouring matter of sanderswood (Pterocarpus santalinus), was procured from Merck of Darmstadt as an amorphous powder. A boiling alcoholic solution of it at once gave a deep maroon-coloured precipitate with potassium acetate. Found, K = 6.94. $C_{30}H_{27}O_{10}K$ requires K = 6.65 per cent.

Santalin has been but little studied, but if the formula $C_{15}H_{14}O_5$ is correct, its potassium salt is formed by the replacement of one hydrogen atom in a double molecule. The reaction was, however, only studied to illustrate its general application, for Merck's preparation was not of guaranteed purity.

Curoumin, the colouring matter of turmeric, gave, in this manner, a deep, blood-red liquid, but no deposit. Jackson and Menke (Amer. Chem. Jour., 4, 77) describe a salt, $C_{14}H_{18}O_4K$, but this cannot be a pure substance, for the formula of curcumin, according to Ciamician and Silber, is $C_{11}H_{20}O_6$ (Ber., 1897, 30, 192).

Rottlerine, as previously shown (Trans., 1895, 67, 230), yields potassium and other derivatives of the formula $C_{88}H_{29}O_9K$, &c., by the action of the alkali carbonates. Qualitative experiments indicated that these could also be prepared from the alkali acetates in the cold.

Vitexin from Vitex littoralis (Trans., 1898, 73, 1021), and scoparin, the

colouring matter of the Spartium scoparium L., do not form insoluble monopotassium derivatives by the action of potassium acetate. Numerous products which are not dyestuffs have been examined, but with negative result, except in the case of hesperitin, $C_{16}H_{14}O_6$ (Trans., 1898, 73, 1035), from which the compounds $(C_{16}H_{14}O_6)_2C_2H_3O_2K$ and $(C_{16}H_{14}O_6)_2C_2H_3O_2Na$ were obtained.

Action of other Salts.

As potassium acetate is so readily decomposed by numerous colouring matters, the action of other salts with morin, quercetin, and alizarin in the presence of alcohol was now studied, they being the most readily obtainable in quantity. The results with quercetin and morin are embodied in the following table; the products obtained from alizarin were not submitted to analysis.

Colouring matter.	Salt employed.	Salt formed.	Found.	Theory.
Quercetin	Potassium carbonate. '', nitrite. '', formate. '', propionate. '', lactate. '', succinate. '', benzoate. '', salicylate. '', benzoate. '', salicylate. '', salicylate. '', salicylate.	C ₁₅ H ₅ O ₇ K C ₁₅ H ₉ O ₇ K ,,	K=11·48 K=11·32 K=11·46 K=11·41 K=11·32 K=11·36 K=11·37 K=11·11 K=11·11 K=11·44 K=11·52 K=11·38	K=11·47 K=11·47

It was considered unnecessary to analyse the samples of monopotassium morin derived from potassium formate, propionate, and lactate. Alizarin readily yielded the crystalline compound $C_{14}H_7O_4K$ when acted on by the above salts in the presence of alcohol, with the exception of potassium lactate and salicylate; with these two, only a deep orange-brown solution was obtained, and no crystals separated at the boiling temperature. Possibly, in these cases, reaction takes place with formation of an additive product of the salt with the colouring matter, as in the case of hesperitin with the alkali acetates, and a compound of this nature appears to be formed with morin and potassium oxalate in the presence of alcohol; the product of the latter reaction separates on cooling as glistening, yellow needles, but contaminated with a trace of morin, from which, owing to its somewhat soluble nature, it can only be freed with difficulty. Analysis gave K = 10.23 and 10.16, and, by decomposition with acid, 81.5 per cent, of

morin, whereas $(C_{15}H_{10}O_7)_2$, $C_2O_4K_2$ requires K=10.07 per cent., and morin 78.1 per cent. When heated, it yields a most voluminous carbon, recalling to mind that obtained from thiocyanate of mercury.

Action of Potassium Acetate in the Cold.—It appeared possible that the production of the above monopotassium salts at the boiling temperature might be preceded in the cold by the formation of an additive product of the colouring matter with the salt employed; this, however, was not the case, for potassium acetate yields with cold alcoholic solutions of morin, quercetin, and alizarin an immediate precipitate of the monometallic derivatives previously described. Respective analyses gave K = 11.28, K = 11.54, K = 14.17 per cent.

Action of Alcoholic Potash.—With the object of preparing the well-known dipotassium alizarin, a boiling solution of the colouring matter in absolute alcohol was treated with alcoholic potash in excess. Crystals at once separated in quantity, which did not appreciably dissolve on adding more alkali. These were collected and washed with alcohol. Found, K=14.05. $C_{14}H_{7}O_{4}K$ requires K=14.02 per cent. This compound was identical with the monopotassium alizarin previously described. The alcoholic filtrate was blue-violet, and contained some dipotassium salt, but for the successful production of the latter the presence of some water appears necessary.

In a similar manner, quercetin gave a crystalline precipitate of the salt $C_{15}H_9O_7K$ (Found, $K=11\cdot52$; theory requires $K=11\cdot47$ per cent.), and a like result was obtained with morin. Found $K=11\cdot32$. $C_{15}H_9O_7K$ requires $K=11\cdot47$. Experiments with anthragallol, purpurin, fisetin, &c., indicated that these behaved similarly. The yield of the mono-derivative in each case was considerable, and there is reason to suspect that, in the entire absence of water, the more saturated compounds cannot be obtained.

Action of Ethylic and Methylic Iodides on the Monopotassium Derivatives of Alizarin, Anthragallol, and Purpurin.

To determine the position of the hydroxyl group in these colouring matters which possesses such strong acid property, the behaviour of the potassium derivatives towards these iodides was studied.

Monopotassium alizarin is not acted on by short digestion with the boiling iodides, and at 151° in the presence of alcohol, alizarin is the main product, when, however, the salt is heated at 230° in sealed tubes with a mixture of carefully dried ethylic iodide and benzene, the desired reaction takes place. The semi-solid, crystalline mass formed on cooling was evaporated to dryness, and extracted with benzene to remove potassium iodide and a trace of the unattacked alizarin derivative. The benzene extracts, on standing, deposited

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orange-coloured needles, which were purified by crystallisation from a mixture of acetic acid and alcohol.

0.1234 gave 0.3236 CO₂ and 0.0537
$$H_2O$$
. $C = 71.51$; $H = 4.83$. $C_{14}H_7O_3(OC_2H_5)$ requires $C = 71.64$; $H = 4.48$ per cent.

It formed orange-coloured needles melting at $187-189^{\circ}$, and on acetylation gave an acetyl compound melting at $139-141^{\circ}$. Evidently it was identical with the alizarin ethyl ether $[OH:OC_2H_5=1:2]$ of Schunck and Marchlewski (Trans., 1894, 65, 185), who give its melting point as $188-189^{\circ}$, and that of its acetyl derivative 141° . The methylation of monopotassium alizarin was carried out in a similar manner, a methyl ether being obtained in the form of orange-coloured needles melting at $224-226^{\circ}$.

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0.1137 gave 0.2950 CO<sub>2</sub> and 0.0440 H<sub>2</sub>O. C=70.76; H=4.29. 0.1925 ,, by Zeisel's method, 0.1775 AgI. CH<sub>3</sub>=5.88. C_{14}H_{7}O_{8}·OCH<sub>3</sub> requires C=70.86; H=3.93; CH<sub>8</sub>=5.90 per cent.
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Two alizarin monomethyl ethers are known, namely, that prepared by Schunck and Marchlewski (*loc. cit.*) melting at 228—229°, and a second, which is present in chay root (Trans., 1893, 63, 1163) and melting at 178—179°. The product obtained seemed to be identical with the first of these two, but, on investigation, its acetyl derivative melted at 196—198°, which is higher than that of Schunck and Marchlewski, namely, 184—186°.

Some alizarin monomethyl ether $[OH:OCH_8=1:2]$ was nowprepared according to one of the methods employed by Liebermann and Jeelinek (*Ber.*, 1888, 21, 1169) for the production of the anthragallol ethers; this consisted in digesting an aqueous alkaline solution of alizarin with methylic iodide for several days. The product, after purification, melted at $224-226^{\circ}$, and its acetyl derivative at $196-198^{\circ}$, and was, therefore, identical with that obtained from monopotassium alizarin.

Monopotassium anthragallol reacts somewhat less readily with ethylic iodide at 230°; the product, which crystallised in glistening, red needles melting at 174—175°, dissolved in alkaline solutions with a red colour, but did not dye mordanted calico. It was thus the anthragallol ethyl ether $[OH:OC_2H_5:OH=1:2:3]$ melting at 175° described by Liebermann and Jeelinek (loc. cit.). These results indicate that the acidic hydroxyl in the anthraquinone colouring matters is in the meta-position relatively to the carbonyl group.

Monopotassium purpurin, when treated with methylic iodide in the same manner, gave a product crystallising from benzene in orange-red needles melting at 228—230°.

0.1063 gave 0.2585 CO₂ and 0.0367 H₂O. C = 66.32; H = 3.83. $C_{14}H_7O_4(OCH_8)$ requires C = 66.66; H = 3.70 per cent.

It is soluble in alkalis with a crimson coloration, bluer than that yielded by purpurin itself, but does not dye mordanted calico. From the preceding results, this purpurin monomethyl ether, not previously prepared, has the constitution $[OH:OC_2H_5:OH=1:2:4]$, and the bluer tone of its alkaline solutions is probably due to the fact that its hydroxyls are similarly placed to those in quinizarin which is soluble in alkalis with a blue colour.

Numerous experiments have been performed with the object of methylating quercetin and morin through their monopotassium derivatives—unfortunately, as yet, with unsatisfactory results. Below 210° no action occurs, and at higher temperatures decomposition ensues to some extent, and three distinct products, one of which is quercetin, have been isolated. Further attempts will be instituted, not only with the above derivatives, but with those of the quercetin glucosides, for the latter, being somewhat soluble in methylic iodide, may react more readily.

Action of Cold Acetic Anhydride on the Potassium Derivatives of Alizarin, Morin, and Quercetin.

The experiments in this direction were first instituted with the object of preparing a monacetyl derivative of alizarin of certain constitution, and subsequently extended to quercetin and morin to determine if these colouring matters reacted in a similar manner.

When monopotassium alizarin (3 grams) is added to cold acetic anhydride (15 grams), the crystals rapidly become orange-red, and no further change is apparent even after 12 hours; the product was collected, drained on a porous tile, and crystallised from a mixture of alcohol and acetic acid. An acetyl determination gave the following result.

1.1480 gave 0.9770 $C_{14}H_8O_4$. Found 85.10. $C_{14}H_7O_4(C_2H_8O)$ requires $C_{14}H_8O_4 = 85.10$ per cent.

Monaestylalizarin crystallises in orange-yellow leaflets melting at 198-201°, and sparingly soluble in alcohol. From its method of preparation, the acetyl group is evidently in the meta-position. In a second experiment, employing similar proportions, it was observed that the monacetyl derivative at first formed is itself attacked on long keeping. The pasty mixture became of thinner consistency, and hard nuclei commenced to form on the side of the vessel, until at length this form of crystal alone was present; after a lapse of three

months (during the summer) these were collected and crystallised from alcohol and acetic acid.

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0.1250 gave 0.3054 CO_2 and 0.0468 H_2O. C = 66.47; H = 4.15.
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1.2316 , 0.9095 $C_{14}H_8O_4$. Found 73.84. $C_{14}H_8O_4(C_9H_8O)_9$ requires C = 66.66; H = 3.70; $C_{14}H_8O_4 = 74.07$ per cent.

The substance melted at 179—183°, and was evidently diacetylalizarin. This result, therefore, shows that alizarin can be fully acetylated in the cold.

Morin.—Previous experiments on the acetylation of morin in the usual manner (Trans., 1896, 69, 792) gives a very soluble product, which crystallises with difficulty, and has not been obtained in a pure condition. The behaviour of alizarin suggested the possibility of a better result by working in the cold. Monopotassium morin dissolves slowly in cold acetic anhydride, but no crystals separate on standing; after 24 hours, the addition of alcohol caused the deposition of a crystalline precipitate, and this was collected, washed with alcohol, and crystallised from a mixture of alcohol and acetic acid.

0.1167 gave 0.2510 CO₂ and 0.0437 H₂O. C = 58.65; H = 4.16.

0.6992, 0.4525 $C_{15}H_{10}O_{7}$.* Found 64.71.

1.0940 , 0.7045 $C_{15}H_{10}O_{7}$. , 64.39.

 $C_{15}H_6O_7(C_2H_8O)_4$ requires C=58.72; H=3.83; $C_{11}H_{10}O_7=64.26$ per cent.

Tetracetylmorin forms colourless, prismatic needles melting at 142—145°, only sparingly soluble in alcohol, but somewhat readily in acetic acid.

From the formation of pentacetyltetrabromomorin and other derivatives of this colouring matter (loc. cit.), the above, although interesting as the only pure acetylmorin as yet obtained, leaves it not fully acetylated. A second experiment showed that if the mixture is kept for 6 weeks, the compound first produced is further attacked, with formation of a very soluble colourless product; this is identical in its nature with that produced when morin is acetylated in the usual manner, and has not yet been obtained pure. Its soluble nature suggests that it is not the pentacetyl derivative, but results from a secondary reaction, being possibly an anhydro-compound, for anhydromorin sulphate, $C_{15}H_8O_6\cdot H_2SO_4$ (Trans., 1895, 67, 649), is produced by sulphuric acid. The action of cold acetic anhydride on

* For determining the composition of the acetylmorin, sulphuric acid could not be employed, as the morin thus formed is partially converted into a sulphonic acid. In the above determinations, the acetyl compound (1 gram approx.), dissolved in 7 c.c. of boiling acetic acid, was treated gradually with 5 c.c. of hydrochloric acid, and the mixture of morin hydrochloride, &c., treated with boiling water, and allowed to stand overnight.

this sulphate gives a colourless, soluble product similar to that above referred to.

Monopotassium quercetin (3 grams) gradually dissolves in cold acetic anhydride (30 grams), and, on standing, crystals separate; after 24 hours, the pasty mass was mixed with alcohol, drained with the aid of the pump, and repeatedly crystallised from a mixture of alcohol and acetic acid. To determine if the compound was homogeneous, five distinct portions were prepared, and three of these analysed.

Triacetylquercetin crystallises from alcohol, in which it is only sparingly soluble, in spongy masses of fine, colourless needles melting at 167—169°.

No simpler acetyl derivative could be obtained in a pure condition from quercetin; such, no doubt, exists in the solution which is first formed, and must be extremely soluble, as the addition of alcohol gives no precipitate. If, however, the mixture is allowed to become hot from the action of the anhydride with the alcohol, crystals of the triacetyl compound rapidly separate, and can thus be produced in a few minutes.

If quercetin sulphate, $C_{15}H_{10}O_7$, H_2SO_4 (3 grams), is added to cold acetic anhydride (20 grams), the solution! which is slowly formed deposits crystals if left overnight, and these increase in quantity on treating the mixture with alcohol. Crystallised from a mixture of alcohol and acetic acid, the product forms silky needles melting at 193—194°.

In the case of the sulphate, therefore, the reaction is more energetic; a tetracetylquercetin is produced.

A cold mixture of quercetin, acetic anhydride, and sodium acetate, the latter in the proportion necessary for the formation of a monosodium derivative, behaved in a manner analogous to monosodium quercetin and acetic anhydride. The product, on decomposition, gave

69.58 per cent. of quercetin, and had properties indicating the above triacetylquercetin. Again, if triacetylquercetin is suspended in acetic anhydride, and a little sulphuric acid added, tetracetylquercetin separates from the solution after a time.

Quercetin itself is not appreciably attacked by cold acetic anhydride if left in contact with it for several days, although in two months at the winter temperature partial acetylation had occurred. The product, which was neither of the above derivatives, was not closely examined.

Although it seems probable that, in the acetylation of quercetin, alizarin, and similar substances, the hydroxyl which decomposes potassium acetate is first attacked by a mixture of acetic anhydride and sodium acetate, the behaviour of the sodium acetate in this reaction is in no way clear. For instance, alizarin methyl ether $[OH:OCH_8=1:2]$ does not decompose alcoholic potassium acetate, and is not acetylated by boiling for 4 hours with acetic anhydride. If sodium acetate, however, is present, the latter reaction rapidly takes place.

It is possible that the employment of this method of acetylation in the cold may be useful for the identification of colouring matters which yield no definite acetyl compound when treated in the usual manner.

THEORETICAL.

The results of this investigation indicate that all the colouring matters of the anthraquinone, and many of those belonging to the flavone, xanthone, and ketone groups, have acid properties which enable them to decompose the alkali salts of various acids. With the exception of morin and rhamnazin, no colouring matter of known constitution is markedly acidic unless it contains two hydroxyls in the ortho-position relatively to one another, and consequently has strong dyeing properties.

The acid nature of these members of the flavone or quercetin group is very interesting, for previously (Trans., 1895, 67, 644, and 1896, 69, 1439) it has been shown that they also possess marked basic properties, forming compounds of the colouring matter with one molecule of a mineral acid. On comparing the results of the former investigations with those of the present work, one is at once struck with the fact that colouring matters of the flavone series which possess basic properties, and those only, have a marked acid nature. Thus chrysin and apigenin yield neither acid compounds nor metallic derivatives by the methods described, and differ in this respect from the other colouring matters of this group which have been examined. Again, rhamnetin and rhamnazin, the methyl ethers of quercetin, form acid compounds with difficulty, and, on the other hand, their behaviour

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towards potassium acetate indicates but feeble acid properties, 2 mols. of each being required for the decomposition of 1 mol. of the acetate. Finally, water exerts a decomposing influence on all acid and basic compounds of the members of this group.

In the so-called flavone derivatives here examined, as many as four to six hydroxyl groups are present, and in each case but one of these has the power of decomposing, under the conditions described, the alkali That this hydroxyl, per se, is strongly acid seems very doubtful, and it is much more probable in view of the decomposition effected by hot water, that the acid reaction is the result of a change in the molecule. In other words, the displacement of the hydrogen in this one hydroxyl group by a metal admits of a change of structure which cannot occur in the colouring matter itself. In former communications dealing with the acid compounds, the formation of there was explained according to the quinonoid theory of coloured compounds (H. E. Armstrong, Proc. Chem. Soc.), and this is also applicable to the metallic derivatives under discussion. Since the publication of this paper (loc. cit.), further work has shown that only those colouring matters (morin and rhamnazin excepted) which contain ortho-hydroxyls have acid and basic properties, and these results have suggested another constitutional formula; the latter (II) and that formerly considered most applicable (I) are here given, and represent monopotassium quercetin.

According to the formula I, the acid compounds can also be obviously represented, quercetin hydrochloride containing the group

as it tends to explain the influence of the methoxy-groups on the acidity and basicity of rhamnetin and rhamnazin.

Feueratein and Kostanecki (Ber., 1898, 31, 1760) have shown that

flavone, the parent substance of this group, is colourless, and it is probable that its yellow derivatives already have the quinonoid constitution I. In the formation of their metallic derivatives and acid compounds, the change represented by formula II occurs, and the production of these is thus assigned to an alteration in the quinonoid form of the dyestuff, which is again reversed by the action of water. The lower members of this series, for instance, chrysin,

are but feebly acid, and poor dyestuffs, properties which apparently go hand in hand, and these are considered as the effect of the quinonoid constitution, I. Although possible, it appears unlikely that the addition of two hydroxyls to chrysin in the positions in which they occur in quercetin would so strongly develop its acid function without their apparently taking part in the effect.

Morin, to which I have provisionally assigned the constitution of a flavone derivative (Trans., 1896, 69, 798), contains no orthohydroxyls, but to its metallic derivatives a quinonoid form can be given, as in the case of quercetin, for it must be remembered that, although in anthraquinone derivatives ortho-hydroxyls confer dyeing property with mordants, it is not so in the flavone group, for chrysin, apigenin, and isorhamnetin are colouring matters. Morin is colourless (Trans., 1895, 67, 650), and this property is considered by Herzig* (Monatsh, 1897, 18, 700) to throw doubt on its flavone constitution (loc. cit.); to this, however, the arguments above employed are considered sufficient answer.

The expression of the acid property of colouring matters of the xanthone and benzophenone groups, as an assumption of or a property of an existing quinonoid arrangement can obviously be readily expressed by formula I. In the latter class, no colouring matters exist which do not contain ortho-hydroxyls.

Alizarin Group.—The colour of the metallic derivatives of alizarin, anthragallol, &c., as described in this paper, differs more markedly

* In his paper, Herzig suggests that Bablich and I omitted to find the water of crystallisation in tetrabromomorin ethyl ether. This substance was merely examined as to the ethoxy-group, and the presence or absence of water of crystallisation was immaterial;

 $C_{17}H_{10}Br_4O_7$ requires $C_2H_6=4.48$; $C_{17}H_{10}BrO_7+H_2O=4.86$. Found 4.56. I am frequently aware of the presence of water of crystallisation under certain conditions in the substances I examine, and if no special interest is thereby affected, ignore or remove this when necessary, before analysis.

from that of the dyestuff themselves than is the case with the yellow colouring matters, being almost as intense as the fully saturated salts. As these, when etherified, show that the acidic hydroxyl is in the paraposition relatively to one of the carbonyl groups, this supports the theory that the formation of these derivatives is accompanied by quinonoid change, again reversed on removal of the metal.

Alizarin methyl ether. Monopotassium alizarin.

An essential feature of this group is the presence of a second hydroxyl in the ortho-position relatively to that necessary for the production of quinonoid change, and this also confers dyeing property. The red monobarium derivative of alizarin described in this paper indicates the occurrence of two classes of coloured compounds, one violet, and a second, which on its formation reverts to the original constitution of alizarin and is red. Quinizarin, C14H2O4 [OH:OH=1:4], contains parahydroxyls, but is soluble in alkalis with a deep blue coloration, if anything, more intense than that given by alizarin itself. This behaviour, which at first sight seems opposed to the explanation suggested above, is readily accounted for on the assumption that the parahydroxyls assume a quinonoid change, and the intense colour of the alkaline solution would thus be due to the presence in quinizarin of two such groups. Its lack of acidic and tinctorial properties points to the fact that this second change is not readily assumed and is of an unstable nature; this appears to be the case, for according to Schunck and Römer (Ber., 1877, 10, 555) the blue alkaline solution is readily decomposed by carbonic acid, whereas that of the alizarin derivative is not. In confirmation of this instability, it was noted that when crystals of dipotassium quinizarin and monopotassium alizarin were placed side by side with free access of air, the alizarin was not affected, but the quinizarin derivative became red from separation of free quinizarin.

The anthraquinone colouring matters have not yielded any acid compounds, but as orange red morindone (trihydroxymethylanthraquinone) and alizarin, for instance, dissolve in sulphuric acid with a deep blue and deep dark red colour respectively, it is likely that these solutions contain unstable acid compounds similar in type to the corresponding flavone derivatives.

Dyeing Properties of the Monopotassium Derivatives of Quercetin and Alizarin.

The employment of calcium acetate to assist in the dyeing of certain phenolic colouring matters is well known, and researches on this point have indicated that the calcium is taken up to form an essential part of the colour lake; the alkali acetates also, although not employed commercially, are known to produce a somewhat similar effect. The reaction here involved appears analogous to the production of the metallic derivatives described in this paper, indicating as probable that the calcium, for instance, in an alizarin lake has partly neutralised the hydroxyl which is in the meta-position relatively to the carbonyl group. Dyeing experiments with the potassium derivative of alizarin and quercetin on aluminium mordanted wool at first sight corroborated this view, in that the shades produced were very similar in character to those given by mixtures of the colouring matter with sodium or calcium acetates; on the other hand, these results were hardly conclusive, owing to the acid nature of the alum mordant, which tends to take up the metal, in part, at all events, during the dyeing operation. With mordanted calico, the effect was hardly comparable, as the percentage of metal in potassium alizarin is in excess of that necessary for successful dyeing, but in further experiments this may be obviated by employing mixtures of this compound and free alizarin. As previously stated, the alkali acetates are not decomposed by the colouring matter in aqueous solution, although as the liquid in the case of alizarin acquires a red tint, an unstable compound of the alizarin and the acetate may exist in the hot solution. The acetates of the alkaline earthy metals, however, are more active, for with a boiling calcium acetate solution, alizarin yields, apparently, first the monocalcium derivative and ultimately, after some hours, the well known calcium alizarin, C14H2O4Ca; by this method, the latter was obtained in glistening needles having a metallic lustre, so far as I am aware, it has previously been obtained only in the amorphous condition. Ca = 14.13. Theory requires Ca = 14.38 per cent. This reaction will be further studied, together with the behaviour of other colouring matters towards the acetates of this group.

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XLIII.—A Method of Studying Polymorphism, and on Polymorphism as the Cause of some Thermal Peculiarities of Chloral Hydrate.

By WILLIAM JACKSON POPE.

In studying the thermochemical behaviour of chloral hydrate, Berthelot made the remarkable discovery that the latent heat of fusion of the freshly solidified substance is only about one-half of that of material solidified several days previously (Ann. chim. phys., 1877, [v], 12, 536). This retention of part of the latent heat of fusion seems at first sight highly anomalous, and Berthelot considers (loc. cit., p. 565) that it may be explained by assuming that the substance remains soft and pasty for some time after solidification, and does not change sharply from the liquid to the solid state. Differences between the latent heat of fusion and of solidification may consequently be attributed either (1) to differences in plasticity, or (2) to differences in crystalline form; this distinction is one of great importance, and but little evidence supporting it has been advanced. I have, therefore, examined the case of chloral hydrate, in which Berthelot attributes the thermal peculiarities to the assumption of a plastic condition on solidification, in order to ascertain whether the distinction made by Berthelot is necessary; the results of the work now brought forward show that the distinction is unnecessary, at any rate in the case of chloral hydrate, the differences in plasticity being due merely to differences in crystalline form.

On melting a few grams of chloral hydrate in a test tube and pouring the liquid on to a slab, it solidifies to what is seen by macroscopic examination to be a felted aggregate of minute needles; the solid mass is somewhat pasty in character, and does not readily crumble between the fingers. On preserving the mass in a stoppered bottle for some days, it becomes more macrocrystalline in character, and loses its felted appearance; it is then much more friable, and crumbles easily between the fingers. In order to obtain the chloral hydrate in a form suitable for crystallographic examination, a little is placed on a microscope slide under a cover-slip, and the slide gently warmed; as soon as fusion has occurred, the cover-slip is pressed down so as to spread the drop of liquid over its whole area and the slide is placed aside to cool. After a few minutes, solidification sets in at some particular point, and then crystallisation rapidly proceeds until the whole is solid. very thin film of the crystalline substance is thus readily obtained free from air-bubbles, and in a form in which it can be exhaustively ex-

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amined in the polarising microscope. The film consists entirely of long, flattened needles, a great proportion of which do not illuminate on rotation in a parallel beam between crossed Nicols; these seem to be uniaxial, the optic axis emerging normally to the plate. Many of the needles, however, illuminate brilliantly between crossed Nicols and show straight extinction; the ends of these are cut off by two symmetrically placed faces. All these acicular crystals seem to be crystallographically similar, although some, probably owing to internal strain, are biaxial. On again examining the section after about 12 hours, a number of diamond-shaped plates are observed distributed about amongst the needles; these are monosymmetric, and show an optic axis emerging obliquely through the large, flat face which is in the plane of symmetry zone. The latter plane is the optic axial plane. As more time elapses, the number and size of these monosymmetric crystals increase, and the quantity of the needles decreases, until after six or seven days the whole preparation becomes converted into the monosymmetric form.

It is thus evident that crystalline chloral hydrate exists in at least two forms, namely, a β -modification, unstable at ordinary temperatures, and crystallising in uniaxial needles, and an α -modification, stable at ordinary temperatures, and crystallising in monosymmetric plates. Further, the change of the β - into the α -modification proceeds slowly, requiring at ordinary atmospheric temperatures several days for its completion.

As is well known, the conversion of one crystalline modification of a substance into another by a fall in temperature is accompanied by development of heat. It is, therefore, hardly to be doubted that the varying latent heat of fusion of chloral hydrate is due to the determinations being made with mixtures in various proportions of a- and β -chloral hydrate; the β -modification necessarily has the smaller latent heat of fusion, and as, at ordinary temperatures, its quantity continuously decreases, the apparent latent heat of fusion continuously increases as time goes on.

Since the β -modification is stable at the higher temperature, it might be expected to revert to the a-modification more readily at low temperatures than at higher ones, and this tendency should make itself apparent by an increased speed of change. This was fully substantiated by experiment; on keeping a freshly solidified film of the β -variety at -18° for 2 hours, a great part of it became converted into the a-modification; the same change would have required at least a day at the ordinary temperature. The increased speed of conversion at low temperatures is easily traced by comparing results obtained during the summer and winter months. Apart from this temperature influence, considerable differences are observed between various

samples of chloral hydrate in the speed of conversion of the β - into the a-modification; these are probably due to the different degrees of impurity of the samples.*

Although it is readily ascertained by microscopic examination that chloral hydrate is dimorphous, yet the interconversion of the two modifications is of so interesting a nature that it was desirable to obtain a method by which the progress of the change of the β - into the a-variety from day to day could be permanently recorded in a manner free from the personal bias inseparable from freehand drawings. This end was simply and satisfactorily accomplished by photographing the microscopic preparations between crossed Nicols. An optical bench was constructed by Messrs. Baird and Tatlock, on which are mounted, in the order named, an incandescent gas lamp, a projection lantern condenser, a polarising microscope with tube arranged horizontally. and, lastly, a quarter-plate camera without a lens; the lamp, condenser, and camera are so arranged as to be optically concentric with the microscope. An ocular may or may not be used in the microscope, but it is preferable to use an ocular, as by so doing a 'flare-spot,' which made its appearance on the ground glass with several microscopes when no eyepiece was used, was eliminated. The crystal preparation to be photographed is placed on the microscope stage, and by simultaneously racking the camera back and the objective backwards and forwards, an image of the required size is focussed on the screen; the slide is then adjusted on the stage until the part to be photographed occupies the field of view. After finally focussing by aid of the fine adjusting screw of the microscope, the picture may be photographed. Using a 1-inch objective of N.A. = 0.25, and a total magnifying power of about 60 diameters, the necessary exposure with an apparatus such as that described is from 3 to 5 minutes; when low powers such as one inch or a half-inch objective is used, all the sub-stage condensing systems are removed, so that the light entering from the polarising Nicol forms a nearly parallel beam; it is also advisable to rotate the Nicols so that their planes of polarisation are horizontal and vertical, in order that the negative and prints shall show at once the direction of extinction in the crystalline fragments. The objects are photographed between crossed Nicols, not only to show the extinction directions, but mainly because the outlines and details of doubly refracting preparations, although nearly invisible in ordinary light, become plainly visible and stand out with great boldness when examined or photographed between crossed Nicols.

^{*} The fact that the degree of impurity of the material seems to affect the speed of interconversion of the α- and β-modifications has led Dr. Armstrong to suggest that the two forms perhaps have the constitutions CCl2 COH, H2O and CCl3 CH(OH)2. Compare W. H. Perkin, sen., Trans., 1887, 51, 808.

The method of obtaining the pictures reproduced in the plates is thus detailed because of its great value as a means of identifying substances. A photomicrograph, taken under definite and stated conditions such as those now described, is highly characteristic in the case of many substances, and, if accompanied by a few lines stating the optical characteristics of the crystalline flakes composing the film, affords a rapid and almost infallible method of judging as to the identity or otherwise of two preparations.

In order, as stated above, to obtain a permanent record of the interconversion of a- and β -chloral hydrate, sets of photomicrographs were taken of various preparations.

A set of photographs depicting the state of chloral hydrate during a period of six days after solidification is found in numbers 1, 2, 3, and 4 of the plate; (p. 464) the magnification is here only 30 diameters. Number 1 consists wholly of the acicular β -modification, and was taken one hour after solidification; in number 2, taken two days later, a few diamond-shaped pieces are observable, but the main bulk of the mass consists of the β -modification. In picture number 3, taken four days after solidification, the diamond-shaped pieces depicted in number 2 are observed to have grown considerably at the expense of the needles. Photograph number 4, taken six days after solidification, shows that after six days the whole mass consisted of the α -variety; other pictures obtained after this stage has been reached show that no further crystallographic change occurs until volatilisation takes place from the sides of the cover-slip.

Crystalline Form of a-Chloral Hydrats.

Many unsuccessful attempts were made to obtain measurable crystals of chloral hydrate by the spontaneous evaporation of solutions in various solvents; these were usually rendered futile by the property of superfusion possessed by chloral hydrate in a marked degree. Slow sublimation in a Sprengel vacuum, which allows of the formation of well-developed crystals of many substances, such as camphor, which cannot be obtained in large crystals from solution, led to the deposition of broad, thin, rhomboidal plates which could not be detached from the sides of the vessel without destroying them. The crystals ultimately found to give the best goniometrical results were obtained by dissolving carefully dried chloral hydrate in purified chloroform, and leaving half a litre or so of the solution to evaporate spontaneously in a flask with a plug of cotton-wool in the neck; one lot of solution thus left at constant temperature yielded a crop of small, brilliant crystals (Fig. 1) of stout habit which gave good results on measurement. These crystals were about 0.5 mm. long, and

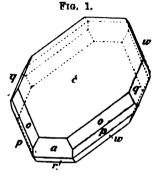
were not at all hygroscopic under ordinary atmospheric conditions the following is their crystallographic description.

Crystalline system.—Monosymmetric.

$$a:b:c=1.6188:1:1.7701.$$

 $\beta=68^{\circ}$ 52'.

Forms present.— $a\{100\}$, $c\{001\}$, $r\{\overline{1}01\}$, $p\{110\}$, $q\{011\}$, $o\{111\}$, and $w\{11\overline{1}\}$.



The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
ac = 100:001	87	68°25′—69°17′	68°49′	68°52′
$cr = 001 : \overline{1}01$	18	59 3 60 1	59 27	59 18
$ar = \bar{1}00:101$	11	51 26 —52 6	51 41	51 50
ao = 100:111	24	52 4 52 54	52 29	52 31
oq = 111:011	89	26 21 —27 11	26 49	26 43
aq = 100:011	17	78 56 79 32	79 17	79 14
$qw = 011 : \overline{1}11$	26	81 48 —32 24	82 6	81 54
$aw = \bar{1}00 : \bar{1}11$	20	68 2969 13	68 44	68 52
ap = 100:110	29	55 57 56 51	56 28	56 29
$pp = 110 : \bar{1}10$	64	66 4867 20	67 2	_
$\infty = 001:111$	59	54 0 - 54 49	54 23	54 18
cp = 001:110	71	78 1 —78 5 7	78 31	
op = 111:110	27	23 41 —24 26	24 8	24 13
$\hat{pw} = 110:11\bar{1}$	17	28 17 —29 11	28 47	28 49
$cw = 00\bar{1} : 11\bar{1}$	69	72 16 —78 4	72 40	
cq = 001:011	44	58 22 —59 11	58 41	58 48
qq = 011:011	21	62 9—63 2	62 87	62 24
$00 = 111 : \bar{1}1\bar{1}$	18	92 15 —98 5	92 41	92 35
$00 = 111 : 1\overline{1}1$	13	86 47 —87 36	87 19	87 25
$rw = \overline{1}01 : \overline{1}11$	16	53 46 54 89	54 12	54 18
$ww = \overline{1}11:11\overline{1}$	8	71 11 —72 0	_71 86	71 24

The form $c\{001\}$ is dominant, and gives very good reflections on the goniometer; the faces of all the other forms are very small and vary in size, but give very good results on measurement. The crystals

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possess a very perfect cleavage parallel to $c\{001\}$, and on examining the crystals conoscopically between crossed Nicols through this form, one optic axis is seen to emerge in the plane of symmetry; the optic axial plane is thus the plane of symmetry, and the obtuse bisectrix, which shows positive double refraction, emerges through c(001). The optic axial angle is fairly small, the double refraction negative, and the dispersion slight.

Measurements of a few angles on chloral hydrate crystals have been published by Groth (Ber., 1872, 5, 675) and des Cloizeaux (Bul. soc. min. franc., 1885, 8, 123); Dufet (Bul. soc. min. franc., 1891, 14, 206) has given more complete measurements, and his values agree very well with those now published, but he did not observe the occurrence of the forms $r\{\bar{1}01\}$ and $q\{011\}$ for which I now give measurements. The axial values arrived at by Dufet and by me are,

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Dufet....... a:b:c=1.61776:1:1.77047. \beta=68^{\circ}49'.
Pope ....... a:b:c=1.6188:1:1.7701. \beta=68^{\circ}52'.
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Localisation of Hygroscopic Power.

One batch of chloral hydrate crystals from a commercial source allowed of some interesting observations respecting hygroscopic power. On exposing a well-developed crystal to the air for a short time, it was observed that, although the faces of the form $c\{001\}$ remained dry and bright for half an hour or more, those of the other forms, $a\{100\}$, $p\{110\}$, $q\{011\}$, $o\{111\}$, and $w\{111\}$, rapidly absorbed moisture and in a few minutes were completely covered with a layer of liquid. No observations seem to have been previously made respecting the variation of hygroscopicity with the direction in crystalline substances, so that the observation that the form $c\{001\}$ absorbs moisture from the air less rapidly than the other forms is the only one on which any views as to the localisation of hygroscopic power can be based, but the observations here recorded are suggestive, and it is obviously of interest to further study the question.

Bromal Hydrate.

Bruner (Compt. rend., 1895, 120, 914), on studying the thermochemical behaviour of bromal hydrate, found that, after fusing and resolidifying, its heat of dissolution is greater than that of bromal hydrate which has not been fused. On dissolution in potash, bromal hydrate which has not been fused evolves +12.08 cals., but one hour after fusion and resolidification it evolves +16.12 cals. It was, therefore, expected that bromal hydrate would be obtainable in two

modifications analogous to those of chloral hydrate, that is to say, that chloral and bromal hydrates would be isodimorphous; curiously enough, however, this is not the case.

A carefully purified specimen of bromal hydrate was dried in a vacuum over calcium chloride, and found to melt quite sharply at 53.5°, and to give, on analysis, numbers corresponding with the composition CBr₂·CH(OH)₂.

0.1941 gave 0.3684 AgBr. Br = 80.10. CBr₂·CH(OH), requires Br = 79.98 per cent.

After fusion on a microscope slide in the manner described above. it readily solidifies from centres to a confusedly radiate mass of much higher double refraction than the β -variety of chloral hydrate. individual crystals scarcely ever extinguish parallel to their directions of growth, and are usually smaller than those of chloral hydrate. In the larger pieces, the acute bisectrix of a biaxial crystal generally emerges obliquely from the face of the plate; the optic axial angle is large, and the crystals are probably monosymmetric. Series of photographs of the film taken at intervals during a period of several weeks indicate that no change of crystalline form occurs, the only slight changes in the character of the mass being such as are attributable to gradual volatilisation. No evidence of dimorphism in bromal hydrate has thus been obtained.

Bromal hydrate is less soluble than the corresponding chloral com pound, and can be obtained in masses of interlaced needles, by cooling the hot solution. The concentrated cold solution, on spontaneous evaporation in a vacuum over calcium chloride, deposits very beautiful, transparent crystals; these are long, hard, brittle prisms possessing high lustre, and belong to the monosymmetric system. After withdrawal from the solution, the crystals are best dried for crystallographic examination with a soft linen cloth; this, it may be mentioned, is perhaps the best way of removing mother liquor from crystals destined for measurement. The crystals may readily be obtained of 8-10 cm. in length and 2-3 cm. in breadth. Carius determinations made on this material show it to have the composition $CBr_3 \cdot CH(OH)_2 + H_2O$.

0.2091 gave 0.3699 AgBr. Br = 75.27.

0.1810 , 0.3204 AgBr. Br = 75.30.

 $CBr_3 \cdot CH(OH)_2 + H_2O$ requires Br = 75.21 per cent.

Crystalline system.—Monosymmetric.

a:b:c=1.7861:1:1.3048.

 $\beta = 58^{\circ} 28'$.

Forms present.—a{100}, c{001}, r{101}, and q{011} aized by GOOG VAT. T.YYV

Fig. 2.



The following angular measurements were obtained.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
ac = 100:001	49	58°11′— 58°46′	58°28′	_
cr = 001 : 101	51	44 58 — 45 32	45 13	_
$ar = 100:10\bar{1}$	47	76 1 — 76 36	76 19	76°19′
aq = 100:011	74	71 3 71 49	71 27	_
$aq = \bar{1}00 : 011$	64	108 20 109 0	108 33	108 33
cq = 001:011	48	52 7 — 5 3 2	52 33	52 33
qq = 011:011	22	74 13 — 75 16	74 49	74 56
$rq = \overline{1}01:011$	8	64 9 — 65 14	64 41	64 88
rq = 101:011	9	114 38 115 47	115 19	115 23

The pinacoid forms $a\{100\}$ and $c\{001\}$ are usually dominant, and give very perfect reflections on measurement; the prism $r\{101\}$ is always small, but gives good results. The dome $q\{011\}$ is very brilliant, and gives trustworthy measurements (Fig. 2).

The optic axial plane is perpendicular to the plane of symmetry, and the acute bisectrix is observed through the face a(100), emerging in the angle $ar(100:10\overline{1})$; the optic axial angle is moderately large, the dispersion slight, and the double refraction negative in sign.

After a few hours exposure to the air, the crystals become opaque, but retain their shape and to a certain extent their lustre, becoming at the same time rather more friable; on microscopic examination, the opaque crystals are seen to be no longer single crystalline individuals, but to be covered with an interlaced mass of tiny needles and to show aggregate polarisation. The fresh, transparent crystals begin to melt at 46°, but do not completely liquefy until 50—52°; after solidification, the substance melts for the second time at 50° but still not sharply, so that its behaviour is altogether that of a mixture. After exposing the powdered substance over calcium chloride in a vacuum for a few days, it melts both for the first and second time at 53.5°; it is therefore evident that the change is due, not to dimorphism, but to loss of water of crystallisation.

No explanation can thus be found, in polymorphism, of Bruner's

statement that bromal hydrate exhibits anomalous thermal behaviour just like chloral hydrate; Bruner, however, does not state whether any precaution was taken to ensure that the bromal hydrate used had the composition $CBr_8 \cdot CH(OH)_2$ and was quite free from the material containing water of crystallisation.

The statement has crept into the literature that bromal hydrate is not isomorphous with chloral hydrate. This has arisen from Löwig's statement (Ann. chim. phys., 1832, [ii], 26, 288) that bromal hydrate crystallises in prisms having the form of copper sulphate; this remark refers to the hydrated material CBr₃·CH(OH)₂+H₂O, which naturally could not be isomorphous with a substance of the composition CCl₃·CH(OH)₉. Attempts were made to obtain crystals of the composition CBr₃·CH(OH)₂ in a form suitable for measurement, by crystallising the dry material from dry chloroform or carbon bisulphide; under these circumstances, large, rhomb-shaped, monosymmetric plates, which melted at 53.5° and closely resembled the crystals of chloral hydrate described above, were obtained. The only form sufficiently well developed for examination is $c\{001\}$; there is perfect cleavage parallel to this form, and an optic axis emerges nearly normally through it, the optic axial plane being the plane of symmetry. It is thus evident that chloral hydrate is isomorphous with bromal hydrate.

Menthol.

In order to ascertain whether the variations in the heats of dissolution of chloral hydrate and bromal hydrate are due to incomplete solidification, Bruner (loc. eit.) examined the behaviour of menthol and thymol, substances which he describes as of a somewhat pasty nature, but found that the latent heats of fusion of these are definite quantities which do not vary with the period elapsing since solidification.

Many attempts were made to cultivate measurable crystals of menthol by crystallisation from various solvents, but these were uniformly unsuccessful, owing to the facility with which the substance remains superfused after evaporation of the solvent.

Fused menthol solidifies easily from centres in very long, narrow needles; these are doubly refracting, but so small that no information as to crystalline form can be obtained by their microscopic examination. As cooling proceeds, a sudden alteration in crystalline structure occurs, and the whole material changes with great rapidity into a confused mass of minute, doubly refracting needles, showing aggregate polarisation, but which are so very small that all attempts to determine their crystallographic properties have been unsuccessful. The change in

crystalline form sets in some five minutes or so after the material solidifies; this allows just sufficient time to photograph the first crystalline modification before its sudden conversion into the second modification takes place. Photographs 5 and 6 were obtained in this manner, and represent the same spot in the film before and after the crystallographic change.

Although menthol, like chloral hydrate, is dimorphous, yet Bruner found no variable thermal constants; the reason of this is obviously that the change of the one form of menthol into the other occurs so readily at ordinary temperatures that Bruner was never able to determine the heat of combustion or of dissolution of the unstable modification.

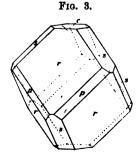
Thymol.

This substance crystallises on spontaneous evaporation of its solution in acetic acid, ethylic acetate, or acetone, in very beautiful, lustrous, transparent, colourless plates; the crystals belong to the rhombohedral system, and exhibit a perfect cleavage parallel to $r\{100\}$. One face of $r\{100\}$ is usually dominant, and this form is always the largest present; the form $s\{110\}$ is smaller, but yet well developed. The basal pinacoid $c\{111\}$ is small, and the prism $p\{\bar{1}10\}$ is not very frequently observed (Fig. 3). All the forms present on the crystals give excellent results on measurement. The double refraction is positive and weak.

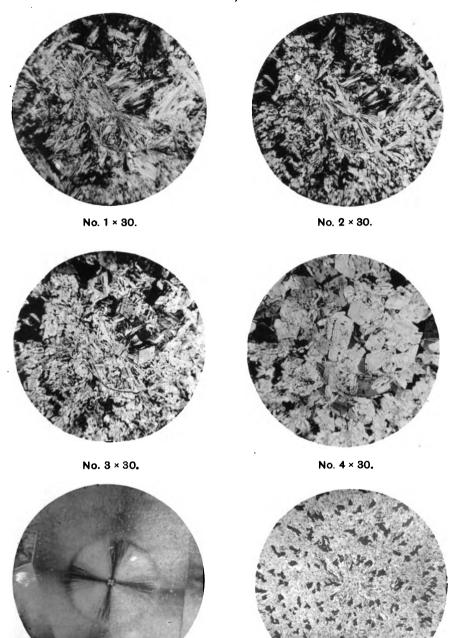
A few angles on crystals of thymol have also been determined by Groth (Ann. Phys. Chem., 1868, 135, 655), and by Miller (Annalen, 1856, 98, 310), but no complete series of measurements has been yet published, and the occurrence of the form $p\{\bar{1}10\}$ has not previously been observed.

Crystalline system.—Hexagonal, Rhombohedral Hemihedrism.

$$a:c=1:1.5679.$$
 $a=79^{\circ} 51' 40''$
Groth ... $a:c=1:1.5685.$ $a=79^{\circ} 52' 30''$



ON POLYMORPHISM, BY W. J. POPE.



No. 5 × 400.

No. 6 × 400.

Forms observed.

C	•••••	{111}	• • • • • • • • • • • • • • • • • • • •	{0001}
7	•••••	{100}	•••••	{10T1}
8	•••••	{110}		$\{01\bar{1}2\}$
p	•••••	{T10}	•••••	{2110}

The following angular measurements were obtained.

Angle.	Number of measure- ments.	Limits.	Mean.	Calcu- lated.	Miller.	Groth.
$cr = 111:100$ $cs = 111:011$ $rs = 100:011$ $rs = \overline{100}:011$ $pr = 10\overline{1}:100$ $rs = 100:010$ $rr = 100:010$ $rr = 100:011$ $pr = 10\overline{1}:01\overline{1}$ $rr = 100:0\overline{10}$ $ps = \overline{110}:011$	24 15 17 21 20 18 12 18 10 9	61° 0'— 61°11' 42 5 — 42 18 103 7 — 103 24 76 37 — 76 51 40 85 — 40 58 49 16 — 49 21 98 33 — 98 40 71 0 — 71 11 59 62 — 60 6 81 5 — 81 26 54 21 — 54 36	61° 6′ 42 10 108 16 76 48 40 43 49 18 98 36 71 6 60 0 81 23 54 28	42°10′ 108 16 76 44 40 42 49 18 98 36·5 71 5·5 60 0 81 23·5 54 27	•••	61°18′ 49 15 98 86

After melting on a microscope slide, the substance crystallises sluggishly, yielding a film which is full of cracks, and consists of large, individual flakes; these plates lie nearly parallel to the optic axis or perpendicular to $c\{111\}$, and, therefore, show negative double refraction. An optic axis is never seen emerging in the field; and the substance does not change in crystalline form if kept, photographs taken immediately after solidification being identical in appearance with pictures taken a month later.

CHEMICAL DEPARTMENT,

CITY AND GUILDS OF LONDON INSTITUTE, CENTRAL TECHNICAL COLLEGE, SOUTH KENSINGTON.

XLIV.—Contribution to the Characterisation of Racemic Compounds.

By A. LADENBURG.

The question whether an inactive substance is a mixture of the active components (d, l, mixture) or a racemic compound (r), has for a long time been open to discussion. I was certainly one of the first who occupied myself with this question, and during the past ten years you. LXXVI.

have frequently taken the opportunity to discuss it (Annalen, 1888, 247, 66; Ber., 1894, 27, 3065; 1895, 28, 163 and 1991; and 1897, 30, 485). Many others have examined and studied thoroughly this problem, however, without being able to arrive at a complete solution.*

Messrs. Kipping and Pope also have lately been studying this problem, and have come to the following conclusion.

"Only one method is at present of really practical use for characterising solid racemic compounds, that, namely, which is based on the determination of the crystalline forms of the optically active and externally compensated materials." This appears to me to be an attack on the views held by myself, and which I have already expressed as follows:—A mixture of enantiomorphic substances may be distinguished from a racemic compound by treating the substance in question, which must contain at least a small surplus of one or the other of the optically active modifications, with inactive substances. If this causes the substance to separate into fractions of different optical activity, it is a racemic compound.

The above-named investigators have tested my statement by experiment, but could not verify it; I, therefore, do not feel capable of maintaining it, but believe that the principle involved in it is correct, and has only been expressed in a misleading manner.

I give my previous statement, therefore, the following form:—To characterise an inactive substance, that is, whether it is a racemic compound, or a mixture of its active components, determine the solubility of the substance without and with the addition of a small quantity of one or the other of its optically active components at the same temperature and with the same solvent. If the solubilities are different, the substance in question is a racemic compound; if the same, it is an enantiomorphic mixture. (Mr. Pope's reply to Professor Ladenburg's statement will be found in the Proceedings, 1899, 15, 73.—[Editor.])

The correctness of this statement seems to me to be indisputable. I have verified it up till now by several examples which I shall continue to augment.†

- 1.—Racemic acid. Solubility in 100 parts of water at 18°.
- * E. Fischer, Ber., 1894, 27, 1525 and 3224; 1896, 29, 2927; Wallach, Ann., 286, 140; Marchlewski, Ber., 1892, 25, 1561; 1895, 28, 1611; Winther, Ber., 1895, 28, 3000; I. Traube, Ber., 1896, 29, 1894; Kipping and Pope, Trans., Chem. Soc., 1897, 71, 989, and 1899, 75, 36; Landolt, Optisches Drehungsvermögen; Walden, Ber., 1896, 29, 1692; Van't Hoff, Ber., 1898, 31, 533; Küster, Ber., 1898, 31, 1847.
- † I desire to expressly state that Van't Hoff ("Bildung und Spaltung von Doppelsalzen") employed the solubility determination with success in the investigation of similar problems (see also Küster).

I. and II. pure racemic acid. III. Racemic acid with an addition of tartaric acid.

- I. 16.590. II. 16.591. III. 18.95.
- 2.—Pyrotartaric acid. Solubilities in 100 parts of water at 13°.
- I. and II. pure pyrotartaric acid. III. The same with an addition of d-pyrotartaric acid.
 - I. 34.83 II. 34.88. III. 38.27.
- 3.—Mixture of d- and l-sodium ammonium tartrats. Solubilities in 100 parts of water at 12:3°.
 - I. Inactive mixture of equal quantities of the two salts.
- II. The same, with the addition of about 8 per cent. of d-sodium ammonium tartrate.
 - I. 43.53. II. 43.41.

By these experiments, it seems to be proved that racemic and pyrotartaric acids are racemic compounds, whilst d- and l-sodium ammonium tartrate remain uncombined in the solution at 12.3°, which is quite in accord with previous experiments.

XLV.—Etherification * Constants of Substituted Acetic Acids.

By John J. Sudborough and Lorenzo L. Lloyd.

The classical researches of Menschutkin have led to several generalisations with regard to the influence of constitution on the rate of etherification of different fatty acids and of different alcohols (Annalen, 1879, 195, 334; 1879, 197, 193; Ann. Chim. Phys., 1881, [v], 23, 14). These indicate, speaking generally, that acids of the type $CR_1R_2R_3 \cdot COOH$, in which $R_1R_2R_3$ are alkyl radicles, are not so readily etherified as acids of the type $CHR_1R_2 \cdot COOH$, and these, in turn less readily than acids of the type $CH_2R \cdot COOH$. The size of the substituting group also plays an important part, as the single large group present in caprylic acid is shown to retard the formation of etheric salt almost as much as the two smaller groups present in isobutyric acid.

The more recent work of Meyer and Sudborough (Ber., 1894, 27, 510, 1580, and 3146), of V. Meyer (Ber., 1895, 28, 182, 1254, 2773, and 3197), of Goldschmidt (Ber., 1895, 28, 3218), and of Kellas (Zeit. physikal. Chem., 1897, 24, 221) on the etherification of substi-

^{* [}The authors prefer the terms "esterification" and "ester," but have consented to "etherification" and "etheric salt" being used in this paper. E. G. D.

tuted benzoic acids, indicates that, in this series also, the amount of etheric salt formed from a given acid largely depends on the constitution of the acid. It has been shown that diortho-substituted benzoic acids vield little or no etheric salt when their alcoholic solutions are treated in the usual manner with dry hydrogen chloride. substituting radicles are large, for example, Cl, Br, I, NO, COOH, no appreciable amount of etheric salt is formed, even when hydrogen chloride is passed through the boiling alcoholic solution for a considerable length of time; on the other hand, when the substituting radicles are relatively small, for example, CH2, OH, or F, small amounts of etheric salt may be obtained under these conditions. relationship between the amount of salt formed and the weight or volume of the substituting group does not appear to be a very simple one, since Kellas has shown that the nitro-group has a greater retarding influence than either bromine or iodine. The results obtained with ortho-substituted benzoic acids indicate that the following groups, Cl, CH₃, Br, I, NO₂ (Kellas), and Br, CH₃, NO₂ (Goldschmidt), stand in the order given as regards their retarding influence. Arranged according to their relative weights, the order would be CH, CI, NO, Br, I, and according to atomic volumes, CH_s, Cl, Br, NO_s, I (compare Graham-Otto I, 3, 449, &c).

Still more recently, we have investigated the series of substituted acrylic acids (Trans., 1897, 73, 81), and here also we have been able to indicate relationships between the constitutions of the various acids and the amount of etheric salt formed; for example, acids of the types,

H·C·X Y·C·COOH' or Z·C·X Y·C·COOH'

are difficult to etherify by the usual method with hydrogen chloride, and a-substituted acrylic acids also are more difficult to etherify than the isomeric β -compounds. The results we have already published were made with acids in which the substituting groups were relatively large, for example, C_6H_5 , I, Br, and Cl; since then, further investigations have been made with methyl derivatives of acrylic acid; the results of these we hope soon to be able to lay before the Society.

The results obtained with substituted benzoic acids indicate that the nature of the substituting group, that is, its positive or negative nature, is of very little influence, as both negative (NO₂, Br, COOH, &c.) and positive (CH₃, &c.) groups cause a retardation. The chief factor appears to be the size of the substituting groups, although, as already stated, it is not clear what is the relationship between the relative weight or volume of the substituting group and its retarding influence.

As interesting results have been obtained in both the benzoic and acrylic acid series, our attention was drawn naturally to the acetic acid series, and we undertook experiments in order to determine whether acids of the general type, OX, X, X, COOH, are not also somewhat difficult to etherify as compared with acetic acid itself. The results obtained by Menschutkin, and already referred to, only apply to alkyl derivatives of acetic acids, and, what is of still greater importance, were obtained without employing a catalytic agent, such as hydrogen chloride; in fact, Menschutkin used the method of etherification usually spoken of now as "autocatalysis." In order that our results might be comparable with those obtained with benzoic and acrylic acids, we determined to employ the hydrogen chloride method and to include halogen, as well as alkyl, derivatives of acetic acid. The only experiments of a general kind, in addition to Menschutkin's, which appear to have been made in this series are those of Lichty (Amer. Chem. Journ., 1895, 17, 27, and 1896, 18, 590), which indicate that, when the autocatalytic method is employed with acetic, chloracetic, dichloracetic, and trichloracetic acids, acetic acid is the least readily, and trichloracetic acid the most readily etherified, although the limits of etherification do not differ to any very great extent.

These results show clearly that, when the autocatalytic method is employed, a broad generalisation with regard to the influence of substituting groups on the retardation of etherification cannot be drawn, as, according to Menschutkin, three methyl groups retard the formation of etheric salt, and, according to Lichty, three chlorine atoms facilitate etherification. We therefore determined to see whether this generalisation held good when hydrogen chloride was introduced as a The acids selected for this purpose were acetic, catalytic agent. propionic, dimethylacetic (isobutyric), trimethylacetic, mono-, di-, and tri-chloracetic, mono-, di-, and tri-bromacetic, iodacetic, tri-iodacetic, phenylacetic, diphenylacetic, dimethylbromacetic (a-bromisobutyric), and methyldibromacetic (aa-dibromopropionic). The method employed in the investigation of the benzoic and acrylic series could not be adopted with these acids, as most of the etheric salts are so readily volatile: the method of direct titration with a standard solution of alkali was therefore used, although it is only applicable at temperatures below 25°, as above this limit part of the hydrogen chloride reacts with the alcohol (methylic alcohol) forming an alkylic chloride with consequent loss of acid (Kellas, loc. cit.).

In none of the other series have the actual etherification constants been determined, merely the amount of etheric salt formed at the end of definite intervals of time when a hydrogen chloride solution of definite strength is employed. Goldschmidt (Ber., 1895, 28, 3218) has shown that, although the reaction between alcohol and acid, in the presence of hydrogen chloride, is bimolecular, yet when a large excess of alcohol is present it may be regarded as monomolecular, and in all the cases which he investigated, an etherification constant could be obtained readily. He has also shown that the velocity of etherification depends on the catalytic agent employed, the constant being almost identical when etherification is brought about either by hydrogen chloride or by hydrogen bromide, but is less when an equivalent quantity of picric acid is employed. In dilute alcoholic solutions, the velocity is proportional to the concentration of the hydrogen chloride.

Still more recently (Zeit. physikal. Chem., 1898, 27, 250), Kistia-kowsky has investigated both the etherification of several fatty acids in mixtures of alcohol and water, and the hydrolysis of the etheric salts of the same acids in mixtures of alcohol and water, by the aid of hydrogen chloride. The results show that, provided the conditions are the same, identical constants are obtained for the etherification of an acid and also for the hydrolysis of its etheric salt, and that in the presence of hydrogen chloride the constants are directly proportional to the amount of hydrogen chloride present. Most interesting of all, from our point of view, is the fact that he has shown that acetic acid has a smaller constant than formic acid, a phenomenon he attributed to the smaller dissociation constant for the former, and further, in the case of the chloracetic acids, that the constants decrease with the increase in the number of chlorine atoms, although the actual constant was established in the case of chloracetic acid alone.

Our results were practically complete when Kistiakowsky's paper appeared, and they confirm, and in many respects amplify, some of his points.

As our experiments were made with pure ethylic alcohol, dried over sodium, we have used the equation for a monomolecular reaction, $K = \frac{1}{t} \log \frac{a}{a-x}$, in which t is the time in hours, and a the initial concentration of the acid.

According to both Goldschmidt and Kistiakowsky, the constant, K, is directly proportional to the amount of hydrogen chloride present, at any rate, in dilute solutions; to confirm this, we have made experiments with phenylacetic acid in ethylic alcohol, using hydrogen chloride of different strengths, namely, N/20, N/40, and N/60. The method adopted was that used in all the other cases, and described on page 471. The strength of the phenylacetic acid solution was practically N/10 in all cases.

The constants found are 0.01494 with N/60 acid, 0.02246 with N/40 acid (see p. 478), and 0.04468 with N/20 acid. Assuming the constant

	A.			В.	
80 c.c. of	lkali to neut	ylic alcohol. required 60 c.c. of ralise the organic		the solution alkali to ner	required 60 c.c. of stralise the organic
in hours.	a - x.	$\frac{1}{t}log_{10}\frac{a}{a-x}.$	t in hours.	a - x.	$\frac{1}{t} log_{10} \frac{a}{a-x}.$
1 2 3 4 5 6	54·1 48·9 44·1 39·8 85·8 82·4	0.0450 0.0444 0.0446 0.0446 0.0449 0.0446 Mean = 0.04468	2 4 6 8 10	56·0 52·8 48·8 45·6 42·6	0.0150 0.0149 0.0150 0.0149 0.0149 Mean = 0.01494

to be proportional to the amount of hydrogen chloride present, the values should be 0.01494, 0.02241, and 0.04482.

The general method we adopted was as follows. In each case, the acid was purified by crystallisation or distillation, and an amount sufficient to give 150 c.c. of N/5 solution was then weighed out. As most of the acids are extremely hygroscopic, they were placed overnight in a desiccator over sulphuric acid, and in the morning dissolved in absolute ethylic alcohol which had been distilled over sodium, the solution being made up to 150 c.c. Two lots of 15 c.c. each were then titrated with N/20 sodium hydroxide solution, using phenolphthalein as an indicator, and the mean of the two results taken. One hundred c.c. of the acid solution was then mixed with 100 c.c. of N/20 HCl in ethylic alcohol which had also been distilled over sodium, so that the solution con-All the experiments were carried out with tained N/40 HCl. N/40 HCl, as it was found that acetic and propionic acids were etherified too readily when stronger solutions were employed. mixture was well shaken for a minute or two in a flask kept as nearly as possible at the same temperature as that at which the actual etherification occurred; quantities of 30 c.c. were then measured from a burette into small bottles of about 150 c.c. capacity, which were afterwards stoppered and placed in a bath at constant temperature. All the bottles employed had been previously filled with concentrated hydrochloric acid, and left for several days to remove any soluble alkalis from the surface of the glass. The bath employed for our determinations was a large sink, through which a stream of water from the main was kept running, and in which the bottles were immersed nearly to their necks. It was found that, for several months in summer, a constant temperature of 14—15° could be maintained. We have taken 14.5° as the mean temperature. During the cooler months, a small stream of warm water was mixed with the cold water passing through the sink, so that the temperature was kept at 14—15°.

At the end of a given time, t, which varied with the different acids, and which could only be determined by actual experiment, one of the bottles was removed, and its contents titrated by first running in N/10 and then finishing the titration with N/20 sodium hydroxide, using phenolphthalein as indicator.

In this way, we obtained the factors required for the equation $K = \frac{1}{t} \log_s \frac{a}{a-x}$; a is the initial concentration of the acid, and may be denoted by the amount of N/20 alkali required to neutralise 15 c.c. of the original acid solution before being mixed with its own volume of N/20 HCl in ethylic alcohol; a-x is the concentration of the acid after the time t, and may be represented by the number of c.c. of alkali (calculated as N/20) required to neutralise the contents of a bottle after remaining for the time t, and subtracting the number of c.c. of N/20 alkali required to neutralise the HCl present. The expression $\frac{1}{t} \log_{10} \frac{a}{a-x}$ can then be readily calculated; this, multiplied by 2·3026 and by 40, gives the etherification constant for the acid at the given temperature when normal hydrogen chloride is employed in ethylic alcoholic solution.

We suggest that the letter E should be used to denote the etherification constant of an organic acid when normal hydrogen chloride is employed. As the constant is proportional to the concentration of the hydrogen chloride, it follows that this constant can be calculated when hydrogen chloride solutions of different strengths are employed. As the constant varies, moreover, with the temperature and also with the different alcohols, we suggest the use of the expressions $E_{\rm MeOH}^{10^{\circ}}$, $E_{\rm toh}^{15^{\circ}}$, &c., to represent the etherification constants, so

that the temperature and the specific alcohol may also be indicated.

The alcohol we employed was Kahlbaum's 99.8 per cent. ethylic alcohol, which we distilled over sodium; its sp. gr. was then

 $d 15.5^{\circ}/15.5^{\circ} = 0.7946.$

In connection with the determination of the constant for tribromacetic acid, we found that when the bottles were left exposed to daylight for several hours, their contents became brownish-red, and on titration a larger amount of acid was found than was originally added; in fact, the amount of acid increased, instead of diminishing with an increase in the length of time during which the solutions were left:—

30 c.c., after 24 hours, required 62.6 c.c. N/20 alkali.

30	"	,,	48	"	,,	65.9	,,	,,	"
3 0	"	,,	96	"	,,	69·1	,,	,,	"
3 0	,,	,,	144	,,	,,	111.3	,,	• ,,	29

This increase in the amount of acid can only be due to the decomposition of the tribromo-acid yielding hydrogen bromide, and, probably, bromine. The decomposition does not occur when the bottles are kept in the dark, as was proved by estimating the amount of hydrogen chloride (+ bromide, if any) after the lapse of several hours. The solution was poured into water acidified with nitric acid, and then precipitated with silver nitrate, when the amount of silver chloride found was practically identical with that required for the hydrogen chloride originally added.

As alcoholic solutions of the tribromo-acid are decomposed so readily when exposed to sunlight, it was considered advisable to conduct the other determinations for halogen acids also in the dark, with, of course, the exception of the final titrations.

A slight difficulty was also met with in titrating the alcoholic solutions of the halogen acids after they had been allowed to remain for some time with the hydrogen chloride solution, as it was found that the pink coloration with the phenolphthalein solution was extremely evanescent, undoubtedly due to the fact that the etheric salts of these acids are hydrolysed so readily by alkalis (see p. 482). The reading taken in all cases was that at which the pink colour remained for 2—3 seconds.

EXPERIMENTAL.

Acetic Acid.—Schuchardt's pure acetic acid melting at 16.5° was submitted twice to fractional distillation, using a fractionating column and collecting the fractions in a Brühl receiver, the air in which was kept dry by the aid of sulphuric acid. The portion boiling at 118° was employed for our experiments, using an alcoholic solution.

	A.			В.	_
	60.4 c.c. N/	20 alkali. solution required	15 c.c. of the alcoholic solution require 60·1 c.c. N/20 alkali. 15 c.c. of the alcoholic solution require 60·2 c.c. N/20 alkali.		
t in hours.	a-x.	$\frac{1}{t}\log\frac{a}{a-x}.$	t in hours.	a-x.	$\frac{1}{t}\log\frac{a}{a-x}.$
1 2 8 4 5	55·1 50·3 45·9 41·9 38·2 84·9	0.0899 0.0897 0.0897 0.0897 0.0898 0.0898	1 2 8 4 5 6	54·9 50·1 45·7 41·7 38·1 84·7	0-0397 0-0397 0-0398 0-0398 0-0397 0-0398

Mean of A and B = 0.3975. $\mathbb{E}_{\mathrm{EtOH}}^{14.5^{\circ}} = 0.03975 \times 40 \times 2.3026 = 8.661.$

Propionic Acid.—Kahlbaum's propionic acid was fractionated in a similar manner to the acetic acid, and the fraction passing over at 140° was employed.

	A.		В.			
15 c.c. required 60 2 c.c. N/20 alkali. 15 c.c. ,, 60 2 c.c. ,, ,,			15 c.c. required 60 c.c. N/20 alkali 15 c.c. ,, 60 c.c. ,, ,,			
t in hours.	a - x.	$\frac{1}{t}\log\frac{a}{a-x}.$	in hours.	a - x.	$\frac{1}{t}\log\frac{a}{a-x}.$	
1.5	53·7 47·9	0·0331 0·0331	1.5	53·4 47·7	0·0337 0·0832	
4·5 6 7·5	42·7 88·1 84·1	0.0831 0.0331 0.0329	4·5 6 7·5	42·5 87·9 34·2	0.0338 0.0338 0.0825	
9	80.2	0.0328	9	80.8	0.0830	

Mean of A and B = 0.0331. $E_{EtOH}^{14.5^{\circ}} = 8.049.$

Isobutyric Acid.—This was twice redistilled, and the portion boiling at 155.5° was used.

	A.			В.	
15 c.c. r 15 c.c.	equired 60°1	c.c. N/20 alkali.	15 c.c. r 15 c.c.	equired 59.8 ,, 59.8	c.c. N/20 alkali. c.c. ,, ,,
in hours.	a - x.	$\frac{1}{t}\log\frac{a}{a-x}.$	t in hours.	a-x.	$\frac{1}{t}log\frac{a}{a-x}.$
2	57·1	0.0111	2	56.8	0.0112
4	54.2	0.0112	4	53.9	0.0113
6	51.6	0.0110	6	51.2	0.0112
8	49.1	0.0110	8	48.8	0.0110
6 8 10	46.8	0.0109	10	46.6	0.0108
12	44.4	0.0110	12	44.2	0.0109

C.

15 c.c.	required	61.0 c.c.	N/20	alkali.
15 c.c.		61 .0 c.c.		,,

t in hours.	a-x.	$\frac{1}{t} \log \frac{a}{a-x}.$
2	57.9	0.0118
4	55.1	0.0110
6	52:3	0.0111
8	49.7	0.0111
12	44.9	0.0111

Mean of A, B, and
$$C = 0.01107$$
.

$$E_{EtOH}^{14.5^{\circ}} = 1.0196.$$

Trimethylacetic Acid.—This acid was prepared by the oxidation of pinacolin by Friedel and Silva's method (Ber., 1873,6,146, and 826), and was purified by repeated fractionation, being finally obtained as a colourless, crystalline solid melting at 35° and boiling at 163.5—164°.

	A.		В.			
15 c.c. required 60°2 c.c. N/20 alkali. 15 c.c. ,, 60°3 c.c. ,, ,, Mean = 60°25.			15 c.c. required 60.0 c.c. N/20 alka 15 c.c. ,, 60.0 c.c. ,, ,,			
t in hours.	a-x.	$\frac{1}{t}\log\frac{a}{a-x}.$	t in hours.	a - x.	$\frac{1}{t}\log\frac{a}{a-x}.$	
6 24 48 72 96 144	59:4 57:1 54:1 51:2 48:6 48:8	0.001028 0.000972 0.000974 0.000982 0.000972 0.000962	24 48 72 96 120 168	56.8 53.7 50.8 48.2 47.5 41.1	0·000992 0·001004 0·001004 0·000991 0·000985 0·000978	

Mean of A and B = 0.000987.

$$E_{\text{EtOH}}^{14.5^{\circ}} = 0.0909.$$

Chloracetic Acid.—This acid was purified by distillation under reduced pressure; it passed over at 104—105° under 20 mm. pressure, and then melted at 63°. Tollens (Ber., 1884, 17, 665) gives 62.5—63.2°.

A.	В.			
15 c.c. required 60.6 c.c. N/20 alkali.	15 c.c. required 60°3 c.c. N/20 alkali.			
15 c.c. , 60 6 c.c, ,,	15 c.c. ,, 60.8 c.c. ,, ,,			

	No. of	t in hours.	a-x.	$\frac{1}{t}log\frac{a}{a-x}$		E ^{14·5°} . EtOH.	
	ments.	Extremes.	Extremes.	Max.	Min.	Mean.	Eton.
A. B.	6 6	1—7 1—6	57·0—39·7 56·7—41·8	0·0266 0·0268	0·0262 0·0264	0.0264	2.432

Dichloracetic Acid.—After fractional distillation, this acid was obtained as a colourless liquid boiling at 190.5°.

- A. 15 c.c. required 59.8 c.c. N/20 alkali.
- B. 15 c.c. , 60·1 c.c. , , , , , , C. 15 c.c. , , , 62·2 c.c. , , , ,

	No. of experi-	t in hours.	a – x.	$\frac{1}{t}\log\frac{a}{a-x}.$			E ^{14.5°} EtOH.
	ments.	Extremes.	Extremes.	Max.	Min.	Mean.	
A. B. C.	5 6 6	48—168 24—168 48—288	55·4—45·6 57·8—46·0 57·6—89·4	0.000705 0.000706 0.000695	0.000691 0.000691 0.000687	0.000695	0.064

Trichloracetic Acid.—This, when purified by distillation under atmospheric pressure, passed over at 195—195.5° under a pressure of 754 mm., and melted at 57°. Clermont gives 55° (Ann. Chim. Phys., 1885, [vi], 6, 135).

A.	В.
15 c.c. required 60.5 c.c. N/20 alkali.	15 c.c. required 60.1 c.c. N/20 alkali.
15 c.c. , 60 5 c.c. , ,	15 c.c. , 60·2 c.c. , ,

_							
	No. of experi-	t in hours.	a-x.		$\frac{1}{t}log\frac{a}{a-x}$		
	ments.	Extremes.	Extremes.	Max.	Min.	Mean	
А. В.	6 6	12—120 24—168	59·8—54·2 58·8—51·6	0.000421 0.000411	0.000398	}0.000408	0.03712

Bromacetic Acid.—This distilled at 117—118° under a pressure of 15 mm., and melted at 49—50°. Kachler gives 50—51° (Monats., 1869, 2, 559).

	15 c.c. req 15 c.c.	A. uired 60°3 c.c. ,, 60°3 c.c.		B. 15 c.c. required 59 9 c.c. N/20 15 c.c. ,, 59 9 c.c. ,,			alkali.	
	No. of experi-	t in hours.	a-x.		$\frac{1}{i}log\frac{a}{a-x}$	•	E.	
	ments.	Extremes.	Extremes.	Max.	Min.	Mean.		
A. B.	6	1-7	57·8—42·7 56·9—44·5	0·0222 0·0223	0.0214 0.0218	0.02165	1.994	

Dibromacetic Acid.—After several distillations under diminished pressure, this was obtained in colourless prisms melting at 48°. Schäffer gives 45—50° (Bor., 1871, 4, 368).

B.

	15 c.c. required 60 1 c.c. N/20 alkali. 15 c.c. ,, 60 1 c.c. ,, ,,			15 c.c. required 59.8 c.c. N/2 15 c.c. ,, 59.8 c.c. ,,			0 alkali.	
	No. of experi-	t in hours.	a - x.		$\frac{1}{t}log\frac{a}{a-x}$	•	E.	
	ments.	Extremes.	Extremes.	Max.	Min.	Mean.		
А. В.	5 5	24—144 24—144	58·8—50·0 57·9—49·7	0.000559 0.000584	0.000550 0.000514	}0.000554	0.051	

Tribromacetic Acid.—As obtained from Kahlbaum, this acid melted at 131°, and even after repeated crystallisation from light petroleum melted at the same temperature. Analysis proved it to be pure. Gal (Annalen, 1864, 129, 56) gives 135°.

	A. 15 c.c. required 60 1 c.c. N/20 alkali. 15 c.c. ,, 60 1 c.c. ,, ,,				B. 15 c.c. required 60 c.c. N/20 alkali 15 c.c. ,, 60 l c.c. ,, ,,				
	No. of experi-	t in hours.	a-x.		$\frac{1}{t}log\frac{a}{a-x}.$		E.		
	ments.	Extremes.	Extremes.	Max.	Min.	Mean.			
А. В.	6 6	24—168 24—168	59·6—56·8 59·6—56·8	0·000151 0·000149	0·000142 0·000136	}0.000148	0.01845		

Iodacetic Acid.—Ethylic iodacetate, obtained by heating ethylic chloracetate with potassium iodide and alcohol, is a colourless liquid boiling at 178—179°, and having an extremely pungent, acrid odour. The ethylic salt was hydrolysed by shaking it in a separating funnel with an excess of concentrated barium hydroxide solution until all the oil had disappeared; the solution was then rendered acid with hydrochloric acid, extracted with ether, and the crude acid obtained on distilling off the ether was purified by crystallisation from light petroleum. It forms long, colourless, prismatic needles melting at 82°.

A.
15 c.c. required 60 4 c.c. N/20 alkali.
15 c.c. ,, 60 4 c.c. ,, ,,

No. of experi-	t in hours.	a-x,	·	$\frac{1}{t}log\frac{a}{a-x}$.			
ments.	Extremes.	Extremes.	Max.	Min.	Mean.		
5	1.2-8	56.6—43.6	0.0190	0.0177	0.0186	1.713	

Triodacetic Acid.—The etherification constant of this acid could not be determined, as, although it dissolves fairly readily in alcohol, the solution immediately becomes deep brown owing to the liberation of iodine; this decomposition takes place even when the solution is kept in the dark.

Phenylacetic Acid.—After several recrystallisations from light petroleum, this acid melted at 76°.

	No. of experi-	t in hours.	a - x.	$\frac{1}{t}log\frac{a}{a-x}$			E.
	ments.	Extremes.	Extremes.	Max.	Min.	Mean.	
А. В.	6	1·5—9 1—8	55.6—37.8 57.2—89.8	0·0226 0·0226	0·0224 0·0222	}0.02246	2.068

Diphenylacetic Acid.—This acid, obtained by reducing benzylic acid with hydriodic acid and phosphorus, was obtained in the form of well-developed, colourless prisms melting at 146°.....Jena (Annales,

1870, 155, 84) gives 145—146°; Friedel and Balsohn (Bull. Soc. Chim., 1880, 33, 590) give 148°.

A.

15 c.c. required 59 9 c.c. N/20 alkali.
15 c.c. ,, 59 7 c.c. ,, ,,

Mean = 59 8.

		В,			
	required				alkali,
15 c,c.	"	60.1	c.c.	,,	**

	No. of experi-	t in hours.	a - x.		$\frac{1}{t}log\frac{a}{a-x}.$		E.
1	ments.	Extremes.	Extremes.	Max.	Min.	Mean.	
A. B.	6 5	24—168 24—168	57·9—47·8 58·1—47·5	0.000619 0.000612	0·000584 0·000608	0.0006065	0.05586

Triphenylacetic Acid.—Heyl and Meyer (Ber., 1895, 28, 2789), who investigated the etherification of this acid with methylic alcohol at its boiling point, have shown that when the boiling alcoholic solution is kept saturated with hydrogen chloride for 3 hours, only 20 per cent. of the theoretical amount of etheric salt is formed. We have not attempted to determine the etherification at 14.5° with N/40 HCl, as from Heyl and Meyer's results, the amount of salt formed under these conditions would be practically nil.

aa-Dibromopropionic Acid, CMeBr₂·COOH.—The crude acid, which we obtained from Schuchardt, was purified by distillation under reduced pressure; the pure acid distils at 126° under a pressure of 20 mm., and then solidifies to colourless crystals melting at 61°. It was found impossible to recrystallise the acid, as it is so readily soluble in all the usual solvents.

		A.			
15 c.c.	required	60.3	c.c.	N/20	alkali.
15 c.c.	,	60.3	G.C.	,,	,,

		В.		•	
	required				alkali.
15 c.c.	"	61.6	c.c.	,,	,,

	No. of experi-	in hours.	a - x.		$\frac{1}{t}log\frac{a}{a-x}$		E.
	ments.	Extremes.	Extremes.	Max.	Min.	Mean.	
A. B.	6	24—168 48—264	59·4—54·2 59·8—52·7	0·000276 0·000268	0.000255 0.000256	0.000263	0.0242

a-Bromisobutyric Acid, CMe₂Br·COOH.—This acid was also purified by distillation under diminished pressure; it passed over at 115°

under 24 mm. pressure, and formed colourless crystals melting at 47—48° and extremely readily soluble in all the usual solvents.

A.	В.
15 c.c. required 60 1 c.c. N/20 alkali.	15 c.c. required 59.8 c.c. N/20 alkali.
15 c.c. ,, 60.0 c.c. ,, ,, Mean = 60.05 .	15 c.c. , 59 8 c.c. ,, ,,

	No. of	t in hours.	a – x.		$\frac{1}{t}log\frac{a}{a-x}$		
	experi- ments	Extremes.	Extremes, corresponding to extremes t.	Max.	Min.	Mean.	E.
А. В.	6 6	12—120 24—168	59·4—58·9 58·5—51·5	0.000894 0.000898	0·000377 0·000386	}0.000387	0-0356

The following table gives a list of the constants found, arranged in descending order, the value K (dissociation constant) is also given where it is known.

Acid.	Formula.	EtoH.	K.
Acetic	СН3.СООН	3.661	0·00180 [O]
Propionic	CH _o Me [•] COOH	8.049	0.00134 [O]
Chloracetic	CH.Cl.COOH	2.432	0.155 [0]
Phenylacetic	CH.Ph·COOH	2.068	1
Bromacetic	CH.Br.COOH	1.994	0.138 [0]
Iodacetic		1.718	0.075 [0]
Isobutyric		1.0196	0.00144 [0]
Frimethylacetic	CMe COOH	0.0909	0.000978 [P]
Dichloracetic	CHCl COOH	0.0840	5.14 [0]
Diphenylacetic	CHPh ₂ ·COOH	0.05586	
Dibromacetic	CHBr. COOH	0.0510	j
Trichloracetic		0.0372	121·0 [O]
a-Bromisobutyric		0.0856	
a-Dibromopropionic		0.0242	8.8 [W]
Tribromacetic	CBr ₂ ·COOH	0.01342	"",

O=Ostwald, Zeit. phys. Chem., 1889, 8, 176. P=Pomeranz, Monats., 1897, 18, 575. W = Walden, Zeit. phys. Chem., 1892, 10, 651.

The following conclusions may be drawn.

1. It appears that all substituted acetic acids have smaller etherification constants than acetic acid itself, when the etherification is brought about by the aid of hydrogen chloride.

A glance at the table indicates that the etherification constant is independent of the strength of the acid, and merely or mainly depends

on the number of substituting groups introduced into the acetic acid molecule, and also on the relative "sizes" of these groups.

These results are interesting when compared with those previously obtained by the autocatalytic method. According to Lichty (loc. cit.), a strong acid, like any of the chloracetic acids, is more readily etherified than a feeble acid, such as acetic; in fact, acetic and the chloracetic acids, when arranged according to their initial velocity of etherification as given by Lichty, follow the same order as when arranged according to their strength, namely, acetic, chloracetic, dichloracetic, trichloracetic. It is then obvious that the two processes of etherification give very different results, since when using hydrogen chloride the main factor is the constitution of the acid, and when no direct catalytic agent is employed the main factor appears to be the strength of the organic acid. Goldschmidt and Kistiakowsky have already drawn attention to the difference in the results obtained by the catalytic and by the autocatalytic methods.

- 2. In a series of substituted acetic acids of the type (a) $\mathrm{CH}_2\mathrm{X}\cdot\mathrm{COOH}$, (b) $\mathrm{CHX}_2\cdot\mathrm{COOH}$, (c) $\mathrm{CX}_3\cdot\mathrm{COOH}$, it appears that the mono-substituted acid is always more readily etherified than the di-substituted acid, and the latter than the tri-substituted acid. This generalisation holds for all the series investigated, namely, methyl-, chlor-, brom-, and phenylacetic acids; it does not, however, always follow that an acid of the type $\mathrm{CX}_3\cdot\mathrm{COOH}$ has a smaller etherification constant than one of the type $\mathrm{CHY}_2\cdot\mathrm{COOH}$. From the table on page 480, it is seen that dichlor-, dibrom-, and diphenyl-acetic acids have lower constants than trimethylacetic acid. It may, however, be taken as a general rule that acids of the type $\mathrm{CX}_1\mathrm{X}_2\mathrm{X}_3\cdot\mathrm{COOH}$ have low etherification constants.
- 3. An interesting point on which our researches throw but little light is the relationship between the retardation of etherification and the size of the group or radicle bringing about the retardation. In the acetic series, it appears that the introduction of a methyl group has the least influence on the lowering of the etherification constant, then follow Cl, Ph, Br, I, but, on the other hand, we have the fact that triphenylacetic acid is not nearly so readily etherified as tribromacetic acid (compare Heyl and Meyer, Ber., 1895, 28, 2789). The question whether the groups CH₃, Cl, C₆H₅, Br, I, &c., when introduced into an acid molecule, always produce a similar effect on the etherification constant, can only be determined by further investigations, which are in progress.

Another interesting point is the remarkable difference between the etherification constants of acids of the benzoic and acetic series. We show in the present communication that the introduction of three bromine atoms in place of three hydrogen atoms in acetic acid reduces the etherification constant to about 1/300th of its original value; in the

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benzoic series, on the other hand, we find that the introduction of two bromine atoms in place of two hydrogen atoms in ortho-positions with respect to the carboxylic groups renders the acid incapable of forming etheric salts. At present, we do not understand why the two atoms in the ortho-positions have an influence so much greater than that of three atoms attached to the carbon atom to which the carboxylic group is directly united; the explanation may perhaps be found in the stereochemistry of the benzene molecule.

Hydrolysis of the Etheric Salts of Substituted Acetic Acids.—V. Meyer (Ber., 1895, 28, 1263) has shown that the etheric salts of diorthosubstituted benzoic acids are much more difficult to hydrolyse than their isomerides, and Kellas (loc. cit.) has shown the same for the etheric salts of ortho-substituted acids. In the latter series, however, it is not always the salt most difficult to form which is most difficult to hydrolyse (compare Wegscheider, Ber., 1895, 28, 2536). The velocity of hydrolysis of various etheric salts of fatty acids has been determined by Reicher (Annalen, 1885, 228, 257), Hemptinne (Zeit. physikal. Chem., 1894, 13, 562), Löwenherz (ibid., 1894, 15, 389), and others, and it is shown that when the hydrolysis is brought about by an acid the results differ from those obtained when an alkali is employed.

As already stated, the recent work of Kistiakowsky shows that the velocity constant of hydrolysis of an etheric salt, R. COOC, H,, by a solution of hydrogen chloride in a mixture of water and alcohol is identical with the etherification constant of the acid R. COOH when an aqueous alcoholic solution of hydrogen chloride of exactly the same concentration is employed. Our results indicate that the latter constant is independent of the strength of the acid, and depends on the constitution or the stereochemistry of the acid molecule. It would necessarily follow that the velocity of hydrolysis is independent of the strength of the organic acid when hydrochloric acid is employed as the hydrolysing agent. That the same remark does not hold good when an alkaline hydrolysing agent is used, is proved by experiments made by Feilmann in conjunction with one of us on the hydrolysis of the etheric salts of substituted acetic acids by the aid of alcoholic potash (Proc., 1897, 13, 241). The results obtained indicate that, of the ethylic salts of methylacetic acids, ethylic acetate is most readily hydrolysed, then follow ethylic propionate, isobutyrate, and trimethylacetate; in other words, in this series the etheric salts which are formed least readily are those which are hydrolysed by sodium hydroxide with the greatest difficulty. The results we obtained with the ethers of halogen acetic acids were quite different. When a N/5 solution of ethylic chloracetate, dichloracetate, trichloracetate, monobromacetate, or tribromacetate in rectified spirit was mixed with an equal volume of N/5 sodium hydroxide, dissolved in rectified spirit, and after some time, the mixture was titrated with N/5 oxalic acid, using phenolphthalein as an indicator, it was found that, in each case, practically the whole of the alkali had disappeared in 10 minutes. The solutions were tested for chloride or bromide, but none was found, thus indicating that the alkali had been employed in hydrolysing the etheric salt. When the N/5 solution of the etheric salt was mixed with twice its volume of the N/5 alkali, and the mixture titrated at the end of 10 minutes, it was found in each case that the amount of alkali used was practically the amount required to hydrolyse the salt; if, instead of being titrated at the end of ten minutes, the mixture was allowed to remain for 1—2 days at the ordinary temperature, then a considerable amount of chloride or bromide was found in the solution, indicating that the excess of alkali had been more or less used up in decomposing the halogen acetic acids.

The only way in which we can account for this ready hydrolysis of the etheric salts of halogen acetic acids is by taking into account the strength of the acids. According to Ostwald's determinations of their electrical conductivities, they are all remarkably strong acids when compared with acetic acid or the fatty acids generally, and this we are forced to consider is the reason why their etheric salts are so readily hydrolysed by alkalis. This consideration may account for the differences previously observed in the hydrolysis of etheric salts with hydrochloric acid and with alkalis. When hydrochloric acid is employed, the hydrolysis will depend mainly on the stereochemistry of the salt molecule (that is, both of the acid and alcohol portion), . and not on the strength of the acid, but when an alkali is employed the strength of the organic acid becomes an important factor, and in certain cases, for example, in the etheric salts of halogen fatty acids becomes the main factor, more or less completely masking the influence of the stereochemistry of the molecule.

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XLVI.—The Rotatory Powers of Optically Active Methoxyand Ethoxy-propionic Acids prepared from Active Lactic Acid.

By Thomas Purdie, F.R.S., and James C. IRVINE, B.Sc.

OBSERVATIONS recently communicated to this Journal (Trans., 1899, 75, 157), showing that ethylic malate and ethylic tartrate are readily converted respectively into ethylic mono- and di-ethoxysuccinate by

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treatment with ethylic iodide and silver oxide, have led us to study the application of alkyl iodides and silver oxide as alkylating agents to the ethereal salts of other hydroxy-acids, and in the following research we give the results obtained with optically active methylic and ethylic lactates.

We have prepared active methylic methoxy- and ethylic ethoxypropionate by this method, and have also made observations on the corresponding acids and their metallic salts, with the view of comparing their activity with that of the same compounds previously obtained (Trans., 1898, '73, 862) by the resolution of the racemic forms.

The d-lactic acid used in our preparations was obtained by the resolution of the inactive acid, as described in previous papers (Trans., 1893, 63, 1143; 1895, 67, 616). The zinc ammonium d-lactate in the hydrated state had the specific rotation -6.06° ($c=8, t=10^{\circ}$), and the d-lactic acid, from which the silver salt used was made, gave a zinc salt containing 12.82 per cent. of water of crystallisation and 23.46 per cent. of zinc, the calculated numbers being 12.88 and 23.41 respectively.

Methylic and Ethylic d-Lactates.

The methylic d-lactate, prepared from the silver salt by J. W. Walker (Trans., 1895, 67, 916), owed its abnormally high specific rotation, $-11\cdot1^{\circ}$, to the presence of small quantities of methoxypropionate (Trans., 1898, 73, 296); that of Frankland and Henderson (Proc., 1895, 11, 54), on the other hand, had a specific rotation of only $-6\cdot80^{\circ}$, and probably contained some of the oppositely active salt. The only other recorded observation is that of Le Bel (Bull. Soc. Chim., 1893, [iii], 9, 674), who gives only the observed rotation, $a=-8\cdot5^{\circ}$ (l=1), of the substance prepared by digesting the alcohol and acid.

We prepared the salt from zinc ammonium d-lactate by the method already described (Trans., 1896, 69, 828) for ethylic lactate. From a mixture of 120 grams of dry salt with 462 grams of methylic alcohol and 96 grams of sulphuric acid, we obtained, after repeated fractionation, 37 grams of methylic lactate (b. p. 58° under 19 mm. pressure), showing the specific rotation, l=1, $a^{20}=-9\cdot01^\circ$, $d=20^\circ/4^\circ=1\cdot0925$, $[a]_{0}^{20}=-8\cdot25^\circ$, a result somewhat higher than that found by Le Bel. Analysis gave:—

C = 45.92; H = 7.86. $C_4H_8O_8$ requires C = 46.15; H = 7.69 per cent.

On distilling a small quantity of the substance at the ordinary pressure, before it was completely fractionated, a dark residue was

left in the flask, and the observed rotation of the distillate rose to -32.5° , a result which may have been due to the presence of moisture and the consequent production of a small quantity of the highly active anhydro-acid or lactide.

The yield obtained by this process was so small that the rest of the material required was prepared by the silver salt method (loc. cit.). From 91 grams of silver d-lactate and 136 grams of methylic iodide, 37 grams of ethereal salt were obtained, boiling at $58-62^{\circ}$ under $22-33^{\circ}$ mm. pressure. The observed rotations of different fractions at about 15° varied from 10.62° to 12.92° (l=1), the fractions of lower boiling point being the more active, a result to be expected from the presence of methoxypropionate.

Ethylic d-lactate was prepared directly from zinc ammonium lactate in the same manner as the methylic salt, the yield and the activity, $a=-11\cdot20^{\circ}$ at 8° (l=1), being nearly the same as in a previous preparation (loc. cit.). The boiling point of the liquid was not very constant, and in the course of repeated distillation under reduced pressure small fractions of slightly higher boiling point were collected, giving a rotation in one instance as high as $-12\cdot1^{\circ}$. As, however, the rotation did not alter after distilling a portion of the main liquid at the ordinary pressure (b. p. $151-152^{\circ}$), and as the mixed more active fractions referred to yielded, on redistillation, a liquid of the lower activity, $a=-10\cdot8^{\circ}$, and a gummy residue, we conclude that the higher activity observed was probably due to the presence of anhydride, and that the specific rotation formerly given for ethylic lactate (loc. cit.) is nearly correct.

Methoxy- and Ethoxy-propionic Acids.

Methylic Lavo-methoxypropionate.—When silver oxide is added slowly to methylic iodide at the ordinary temperature, only a slight reaction occurs, the temperature rising a few degrees on each addition. When methylic lactate, however, is added to the mixture, it rapidly becomes warm and boils violently. In our experiments, the oxide was added gradually to the mixture of lactate with iodide, the proportions used being oxide ($1\frac{1}{3}$ mols.), iodide (3 mols.), and lactate (1 mol.). The reaction was moderated by occasional cooling, and completed by heating for some time on a water-bath. The product, having been diluted with dry ether and filtered, was distilled under reduced pressure and fractionated until the rotation was constant. The crude distillate, obtained after boiling off the ether, amounted to 65 per cent. of the yield calculated for methylic methoxypropionate, and gave in different preparations the observed rotations $-90\cdot25^{\circ}$, $-95\cdot18^{\circ}$, and $-93\cdot73^{\circ}$ (l=1). Practically no lactate was left unacted on, as the liquid, after

being shaken with a dilute solution of potassium hydroxide, dried with anhydrous sodium sulphate and redistilled, showed no increase of activity. The product, after fractional distillation, boiled at 45° under 22 mm. pressure, and on analysis gave;—

I.
$$C = 50.79$$
; $H = 8.63$. II. $C = 50.67$; $H = 8.61$. $C_5H_{10}O_8$ requires $C = 50.84$; $H = 8.47$ per cent.

The optical observations made on this and the other substances described are given below.

Lavo-methoxypropionic acid.—The acid was prepared from the methylic salt by the method previously indicated in the case of the inactive form (Trans., 1898, 73, 869). In order to observe its activity in the anhydrous state, the liquid, after being dried in a vacuum, was distilled. It boiled without decomposition at 108—110° under 30 mm, pressure. The substance was a thick, colourless, pleasant-smelling liquid, which, on analysis, gave

$$C = 46.03$$
; $H = 7.70$.
 $C_4H_8O_8$ requires $C = 46.15$; $H = 7.69$ per cent.

The activity of the acid was unaltered after distilling a second time, and moreover, was proved to be unaffected on distillation by the fact that the rotations of the aqueous solutions of the distilled and undistilled acid, which are quoted later, were nearly the same.

Ethylic Lavo-methoxypropianate.—The substance was obtained by the action of ethylic iodide on the silver salt. An analysis of the liquid (b. p. 46° under 12 mm. pressure) gave:—

$$C = 54.49$$
; $H = 9.23$.
 $C_6H_{12}O_8$ requires $C = 54.55$; $H = 9.09$ per cent.

The substance, however, was probably not quite pure, as owing to its small quantity it could be only once distilled. The specific gravity of the inactive compound (*Annalen*, 1879, 197, 21) is considerably higher than that given below. The rotation found must, therefore, probably be regarded only as approximate.

Ethylic Lavo-ethoxypropionate.—This substance was prepared from ethylic d-lactate in the same manner as methylic methoxypropionate from methylic lactate but the iodide used amounted to only a little in excess of 1 mol., and the product on combustion gave results which indicated the presence of unaltered lactate. As this was not removed by fractional distillation or by treatment with water, the oily liquid was shaken with a cold 5 per cent. aqueous solution of potassium hydroxide, dried with anhydrous sodium sulphate, and redistilled. This treatment raised the rotation about 6°, and the liquid (b. p. 58.5—60°

under 16—19 mm, pressure) now gave results on analysis in agreement with the calculated numbers.

Found I.
$$C = 57.54$$
; $H = 9.25$. II. $C = 57.61$; $H = 9.65$. $C_v H_{14} O_3$ requires $C = 57.53$; $H = 9.59$ per cent.

The crude ethereal salt weighed rather more than the lactate used, and the unaltered lactate contained in it, calculated from the rotations, amounted to about 10 per cent., so that, were a larger proportion of iodide used, a nearly theoretical yield would probably be obtained.

Lavo-ethoxypropionic Acid.—The acid was prepared from the ethylic salt in the same manner as the methoxy-acid from its methylic salt. Before attempting to obtain the acid in the anhydrous state by distillation in a vacuum, an experiment was first made with the inactive acid, which is known to decompose to some extent when distilled at ordinary pressure (Annalen, 1860, 114, 207). This distilled at 131—133° under 63—68 mm. pressure, and the following analysis shows that it does not decompose under these conditions.

Found
$$C = 50.68$$
; $H = 8.21$.
 $C_5H_{10}O_8$ requires $C = 50.85$; $H = 8.47$ per cent.

The active acid was, therefore, similarly treated. It distilled at $105-106^{\circ}$ under 16-19 mm. pressure, as a colourless syrup, which, on combustion, gave C=50.72; H=8.74 per cent. The observations on aqueous solutions of the acid, quoted below, show that its activity is not impaired by distillation.

Methylic Lavo-ethoxypropionate.—The substance was prepared from methylic iodide and silver ethoxypropionate. The liquid had the boiling point 40—41° under 10 mm. pressure, and on analysis gave:—

$$C=54.42$$
; $H=9.15$.
 $C_aH_{10}O_a$ requires $C=54.55$; $H=9.09$ per cent.

With regard to the purity of the substance, the remarks made respecting ethylic methoxypropionate apply in this case also.

The rotations of the substances described were as follows:-

	I.	a ²⁰ °.	d 20°/4°	[a]20°	[a] ^{20°} M/100.
Methoxypropionic acid Methylic methoxypropionate Ethylic methoxypropionate Ethoxypropionic acid Methylic ethoxypropionate Ethylic ethoxypropionate	0.2	-41·16° 95·21 43·02 34·49 39·21 74·55	1.0908 0.9967 0.9551 1.0895 0.9610 0.9355	- 75·47° 95·53 90·08 66·36 81·60 79·69	-78·49° 112·78 118·91 78·30 107·71 116·35

The following observations were also made at other temperatures in a 1 dm. tube.

Methylic methoxypropionate.

$$[\alpha]^{10^{\circ}} = -97.60^{\circ}, d \ 10^{\circ}/4^{\circ} = 0.9994, [\alpha]_{D}^{10^{\circ}} = -97.66^{\circ}.$$

 $[\alpha]^{15^{\circ}} = -96.28^{\circ}, d \ 15^{\circ}/4^{\circ} = 0.9982, [\alpha]_{D}^{10^{\circ}} = -96.45^{\circ}.$

Ethylic ethoxypropionate.

$$[a]^{180} = -75.72^{\circ}, d \ 13^{\circ}/4^{\circ} = 0.9430, [a]_{D}^{180} = -80.30^{\circ}.$$

The specific rotations, therefore, decrease with rise of temperature.

With respect to the accuracy of the rotations found, that of ethylic ethoxypropionate may be a little too low, an insufficient excess of iodide having been used in its preparation, and, as has been already stated, the numbers given for the ethylic methoxy- and methylic ethoxy-salts are only approximate. The following conclusions, however, may be drawn from the observations.

The direct alkylation of the active ethereal lactates produces a remarkable rise of the rotation without altering its sign, the introduction of methyl into the hydroxyl group of methylic lactate, for example, raising the molecular rotation from 8.58° to 112.73°. The results thus confirm the conclusion previously arrived at, that the high activity of the alkyl lactates, prepared from silver lactate, is due to the production of small quantities of alkyloxypropionates.

A comparison of the rotations of the two anhydrous acids and their ethereal salts shows that the introduction of an alkyl radicle into the carboxyl group is attended with a great increase of activity. The substitution of ethyl for methyl in the carboxyl radicle, which raises the activity in the case of the lactates, whether the observed rotation, the specific rotation, or the molecular rotation be taken as its measure, lowers the first two of these constants and raises only the last in the case of the alkyloxypropionates; the same relation subsists between the ethereal malates and alkyloxysuccinates, and also between ethereal lactates and malates and their acetyl derivatives. The substitution of an ethoxy- for a methoxy-group in direct union with the asymmetric carbon atom, on the other hand, causes a fall even in the molecular rotation of both the methylic and the ethylic salts, and a similar effect is exhibited in the specific rotations of the anhydrous acids, although in this case the molecular rotations are about equal. This result is not what was to be expected from previous observations on aqueous solutions of the metallic salts of the same acids, prepared by resolution of the racemoid forms (loc. cit.), as these showed that the ethoxypropionates were more active than the corresponding methoxy-salts in solutions of equivalent concentration. It seemed, therefore, desirable to examine aqueous solutions of the metallic salts of the two acids obtained from active lactic acid, as described above. Aqueous solutions of the acids were also com-

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pared, as the results previously found for methoxypropionic acid were unreliable.

Rotatory Powers of Methoxy- and Ethoxy-propionic Acids and of their Metallic Salts in Aqueous Solution.

The concentrations of the solutions of the acids were ascertained by titration with a decinormal solution of barium hydroxide. As the salts, with the exception of calcium ethoxypropionate, cannot be obtained in a state of definite hydration, and as their complete dehydration involved the risk of racemisation, the concentrations of the solutions were determined by estimating the metals in the residues left after the evaporation of known volumes; the results of these analyses, in percentage numbers, are given below.

The sodium and calcium salts were similar in appearance to those of the active acids obtained by resolution of the racemic forms.

Methoxypropionates.

Sodium salt.--Found, 18.27; calculated, 18.25.

Calcium salt.—Found, 16.21; calculated, 16.26.

Barium salt.—Very soluble, radiating needles. Found, 40.06; calculated, 39.94.

Zinc salt.—A gum crystallising with difficulty in rectangular plates. Found, 23.81; calculated, 24.10.

Magnesium salt.—Very soluble, microscopic prisms. The salt was not constant in weight at 120°, and it then contained about 1 per cent. over the calculated quantity of magnesium.

Ethoxypropionates.

Sodium salt.—Found, 16.54; calculated, 16.43.

Calcium salt.—Found, $H_2O = 11.55$; Ca in anhydrous salt = 14.65; calculated, $2H_2O = 11.61$; Ca = 14.60.

Magnesium salt.—A gum, which could not be freed from water without decomposition.

Zinc salt.—A gum, solidifying to a glassy mass which, when dried at 120° , gave $Zn = 22 \cdot 12$; calculated, $21 \cdot 84$ per cent.

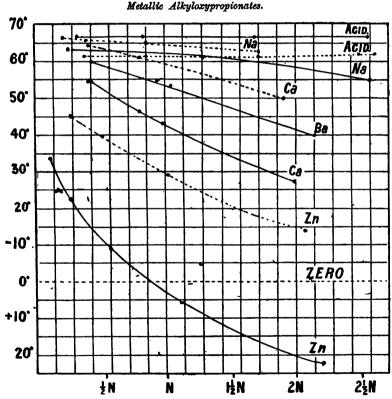
The respective concentrations of the solutions of the two acids and their corresponding salts are approximately equivalent, with the one exception that the solution of the sodium methoxypropionate has a onsiderably higher molecular concentration than that of the ethoxy-compound. The molecular concentrations of the different salts are also, for the most part, comparable with each other. The observations were made at 20°, and in a 1 dm. tube unless the rotations were small, when a 2 dm. or 4 dm. tube was employed. For the sake of brevity, the molecular rotations only are given. In the column headed N, the concentrations are expressed in fractions of a normal solution.

	l-Metho	жургор	ionic Acid.	1-Ethoxypropionic Acid.			
	c. N.		[a]20° M/100.	c.	N.	[a] _b ^{20°} M/100	
Acid	26.726	2.57	- 66·6°	30.572	2.59	- 61·5°	
	17.552	1.69	66.5	20.122	1.70	60.5	
ļ	8.776	0.84	66.4	10.061	0.82	60.6	
	8.210	0.34	66.4	4.025	0.84	61.0	
,, (distilled)	8.522	0.82	66.1	9.612	0.81	60.6	
Sodium salt	82.460	2.58	54.5	28.700	1.69	62·1	
	16.230	1.29	60.1	11.850	0.84	64.7	
	6.492	0.2	61.2	4.740	0.84	65-9	
	3.212	0.25	62.8	2.396	0.17	66.6	
Calcium salt	24.095	1.96	27-7	26.790	1-96	50-2	
	12.0475	0.98	42.7	-	-	—	
	9.6380	0.78	47.1	10.716	0.78	60.9	
	4.8190	0.89	53.6	5.358	0.39	64.1	
Barium salt	86.580	2.18	89 .7		_	_	
	18.290	1.06	53.8	_	_	 	
	7.816	0.48	59 ·8	_	_		
	8.658	0.21	65-2	_	-	-	
Magnesium salt	21 .9760	1.91	85-2	20.984	1.62	51.9	
	10.9880	0.96	43.8	10.482	0.81	55.0	
	5.4940	0.48	47.8	5-241	0.40	57.4	
Zinc salt	29.96	2.21	+ 28 · 1	80.972	2.07	14.0	
	14.98	1.10	+6.2	15.486	1.08	28.9	
	7:49	0.55	-8.2	7.748	0.21	89.1	
	3.745	0.28	- 22 · 1	8.8715	0.25	44.8	
	1.8725	0.14	83.3	_		_	

The molecular rotations are somewhat lower than those previously found, the difference being partly due to the higher temperature at which they were observed, but on the whole the numbers exhibit the same relations. We believe the numbers now given for the methoxyacid are correct, as on recovering it from its salts, the rotation was found to be unaltered. The molecular rotations of the salts increase in every case in the lavo-direction with dilution, and the order of the values found in the most dilute solutions is such as might be expected from the probable degree of electrolytic dissociation, the order of decreasing values for the salts of both acids being sodium, barium, calcium, magnesium, zinc. On plotting the results in curves (see diagram), the abscissæ representing molecular concentrations and the ordinates molecular rotations, it is seen that the magnesium and zinc salts, like the other salts previously examined, conform in general to the law of Oudemans and Landolt, the rotations of the zinc salts increasing very rapidly with dilution. The curves of the methoxy-

propionates lie invariably below those of the corresponding ethoxysalts, and excepting those of the nearly completely dissociated sodium salts, which are parallel, they are in general much steeper.

This is particularly noticeable in the case of the presumably least dissociated zinc salts, the rotation of zinc methoxypropionate passing in a remarkable manner from +23·15° in a 2·2N solution to -33·34° in a 0·14N solution. It is evident that the cause which lowers the rotations of the barium, calcium, and more particularly of the zinc, salts in the more concentrated solutions, whether it be retarded electrolytic dissociation or molecular association or some other factor, has a greater effect on the methoxy-than on the ethoxy-salts.



Note.—Dotted lines represent ethoxy-compounds. The magnesium salts have been omitted.

A comparison of the sodium salts in dilute solution shows that the ethoxy-ion is decidedly more active than the methoxy-ion, our previous results being thus confirmed.

The curves of the acids are nearly horizontal for the range of concentrations examined, but the higher rotations of the anhydrous substances show that the first addition of water must produce a considerable fall, and that this is probably due to the breaking up of molecular aggregates of higher activity than the single molecules or The rotatory powers of the single molecules can, in fact, be very little higher than that of the ions, as in a 26 per cent. solution, which must be very far from a state of complete electrolytic dissociation, the rotatory power of the methoxy-acid approaches that of its sodium salt. In contradistinction to the relation which prevails in the salts, the curve of the methoxy-acid is the higher of the two, the explanation of the anomaly probably being that the methoxy-acid, like its salts, is more subject to molecular aggregation than its homologue. It may be noted that the ethoxy-acid presents an exception to the general law that the change of rotation produced by dilution is always in the direction of the ionic rotation; the rotation of the sodium salt in a 23.7 per cent. solution is already above that of the acid, and the same remark applies to the calcium salt in dilute solution.

If, then, ionic rotations are considered the most reliable measure of activity and molecular rotations are compared throughout, the ethoxy-molecule is the more active of the two, and the greater activity of the methoxy-molecule in the condition of aqueous acid or ethereal salt is due to its greater tendency to form molecular aggregates of higher activity. If, on the other hand, specific rotations, calculated for the ion in the case of metallic salts, be compared, the relations are somewhat simpler. The methoxy-molecule is then the more active of the two, whether in the ethereal salts, anhydrous and aqueous acids, or the fully dissociated sodium salts; the fact that the specific rotations of the methoxypropionates of divalent metals are less than those of the corresponding ethoxy-compounds may be explained on the assumption that they are less dissociated.

In the case of methoxy- and ethoxy-succinic acid, the methoxy- as compared with the ethoxy-group has a similar effect in lowering the rotations of the salts. The specific rotations of the acids, which vary little with concentration, are both about 33°; those of the ions calculated from the normal alkali salts are 14.86° and 22.41° respectively, and the effect is still more pronounced in the salts of the divalent metals.

Some observations have been made on the effect of alcohol and varying temperature on the rotations of the salts. Calcium ethoxypropionate in alcoholic solution undergoes a still more striking fall in rotation than the sodium salt, which we examined previously. Thus the specific rotations $-44\cdot42^{\circ}$ ($c=10\cdot716$) and $-46\cdot75^{\circ}$ ($c=5\cdot358$), determined in aqueous solution, become in alcohol $-9\cdot53^{\circ}$ ($c=11\cdot02$)

and -10.34° (c=5.51). The rotation of the methoxy-acid, like that of its homologue, is raised by alcohol. The following observations show that the rotation of calcium ethoxypropionate falls with rise of temperature, and that its behaviour therefore is not in accordance with the general rule, that rise of temperature and dilution produce similar effects.

$$p = 24.434$$
, $d 10^{\circ}/4^{\circ} = 1.0993$, $[a]_{D}^{10^{\circ}} = -37.75^{\circ}$
 $d 30^{\circ}/4^{\circ} = 1.0912$, $[a]_{D}^{30^{\circ}} = -35.48$.

To the distinctive points in the optical behaviour of lactic and the alkyloxypropionic acids previously indicated (Trans., 1898, 73, 877; 1899, 75, 160), we may now add the phenomena exhibited by the zinc and magnesium salts. A N/10 solution of zinc lactate, despite its comparatively slight electrolytic dissociation, gives a rotation which is not much short of the maximum rotation of the alkali salts; the rotations of the zinc alkyloxypropionates at similar concentration, though increasing rapidly, are still far short of the maximum. The molecular rotations of the lactates of the zinc group increase with molecular weight; the converse nolds true for the alkyloxypropionates.

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XLVII.—Position-Isomerism and Optical Activity. The Comparative Rotatory Powers of Methylic and Ethylic Ditoluylglycerates.

By PERCY FRANKLAND, F.R.S., and HENRY ASTON, Late Priestley and Forster Scholar in Mason University College, Birmingham.

THE influence of position-isomerism in the benzene ring on the rotatory power of optically active substances has formed the subject of several previous investigations by one of us, as well as by other workers (for summary of results in this connection, see P. Frankland and McCrae, Trans., 1898, 73, 307; also P. Frankland and Wharton, Trans., 1896, 69, 1309, 1583; 1899, 75, 337). The present paper deals with the preparation and rotatory properties of the methylic and ethylic salts of the three isomeric ditoluylglyceric acids, which are also compared with the methylic and ethylic salts of dibenzoylglyceric acid previously prepared by P. Frankland and MacGregor (Trans., 1896, 69, 104).

The ethereal salts in question were respectively prepared by the action of the three isomeric toluic chlorides on methylic and VOL. LXXV.

ethylic glycerates. The toluic chlorides were all prepared by the action of phosphorus trichloride at 120—170° on the corresponding toluic acids; they had the following properties:—

Paratoluic chloride (from paratoluic acid, m. p. 178.3°), boiled at 102° under 15 mm. pressure in one preparation, and at 108° under 15 mm. pressure in a second, in which the boiling point was taken in a different flask and with another gauge.

Orthotoluic chlorids (from orthotoluic acid, m. p. 102°), boiled at 99-100° under 14 mm. pressure in one preparation, and at 103° in another, in which a different flask and gauge were employed.

Metatoluic chloride (from metatoluic scid, m. p. 109.5—110°), boiled at 109° under 15 mm. pressure.

Methylic Diparatoluylglycerate (Inactive).

Inactive methylic glycerate (15 grams) was gradually added to twice the calculated quantity of paratoluic chloride (78 grams) at 120—150°. After removing excess of acid chloride by distillation, the residue was dissolved in ether and washed with an aqueous solution of sodium carbonate. The ethereal solution, after drying with calcium chloride, was allowed to evaporate. The resulting crystals were dissolved in benzene, precipitated with light petroleum, and exhibited a final melting point of 98°.

I. 0·2068 gave 0·5116 CO_2 and 0·1033 H_2O . C = 67·47; H = 5·55. II. 0·2013 ,, 0·4982 CO_2 ,, 0·0993 H_2O . C = 67·49; H = 5·48. $C_{20}H_{20}O_6$ requires C = 67·42; H = 5·62 per cent.

The following density determinations were made :-

$$d 99.5^{\circ}/4^{\circ} = 1.1170$$
; $d 116^{\circ}/4^{\circ} = 1.1055$; $d 134^{\circ}/4^{\circ} = 1.0915$.

Methylic Diparatoluylglycerate (Active).

This was prepared from active methylic glycerate ($a_D = -6.06$, l = 1) in the same manner as described above for the inactive compound. The final melting point of the crystalline product was 102°.

I. 0.2007 gave 0.4964 CO₂ and 0.0993 H₂O. C = 67.45; H = 5.49. II. 0.2077 ,, 0.5133 CO₂ ,, 0.1018 H₂O. C = 67.40; H = 5.44. $C_{20}H_{20}O_6$ requires C = 67.42; H = 5.62 per cent.

The density determinations gave:

$$d77^{\circ}/4^{\circ} = 1.1411$$
; $d99^{\circ}/4^{\circ} = 1.1193$; $d117^{\circ}/4^{\circ} = 1.1032$; $d133.3^{\circ}/4^{\circ} = 1.0872$,

and the following polarimetric observations were made:-

Rotation of methylic diparatoluylglycerate.

	Observed rotation, an,		
Temperature.	in 49.85 mm. tube.	$d t^{\circ}/4^{\circ}$.	[a] _{D.}
51.50	+ 20·03°	1.1645	+ 34·50°
78 ·5	+16.33	1.1395	+ 28.75
99-0	+14.13	1.1204	+ 25.30
109.0	+12.83	1.1110	+ 23.16
137.0	+10.03	1.0844	+ 18.55

Ethylic Diparatoluylglycerate (Active).

This was similarly prepared to the methylic compound. Precipitation from benzene by light petroleum, however, only gave the substance as an oil; but on dissolving the latter in alcohol, it was obtained crystalline. The final melting point was 69°.

I. 0.2010 gave 0.5022
$$CO_2$$
 and 0.1055 H_2O . $C = 68.14$; $H = 5.83$.
II. 0.2016 , 0.5034 CO_2 , 0.1055 H_2O . $C = 68.10$; $H = 5.81$.
 $C_{01}H_{02}O_6$ requires $C = 68.11$; $H = 5.95$ per cent.

The density determinations gave:

$$d 66^{\circ}/4^{\circ} = 1.1239$$
; $d 84^{\circ}/4^{\circ} = 1.1076$; $d 100^{\circ}/4^{\circ} = 1.0952$;
 $d .110^{\circ}/4^{\circ} = 1.0861$; $d 129.5^{\circ}/4^{\circ} = 1.0694$,

and the following polarimetric observations were made :-

Rotation of ethylic diparatoluylglycerate.

	Observed rotation, an,		
Temperature.		d t°/4°.	[a] _D
16·5°	+ 25·10°	1.1665	+43·10°
52·5	+20.42	1.1355	+ 36.01
76.5	+17.38	1.1150	+31.09
99.9	+14.32	1.0953	+26.19
110.0	+ 13.10	1.0861	+24.16
140.5	+9.62	1.0598	+ 18.18

Methylic Dimetatoluylglycerate (Active).

The method of preparation was similar to that described above. On precipitating the benzene solution with light petroleum, the substance was obtained as an oil, which could not be induced to solidify. The process of dissolving in benzene and precipitating with light petroleum was repeated until the product had a constant rotation.

I. 0.2040 gave 0.5035 CO_2 and 0.1012 H_2O . C = 67.31; H = 5.51. II. 0.1989 ,, 0.4922 CO_2 ,, 0.0989 H_2O . C = 67.49; H = 5.52. $C_{90}H_{90}O_6$ requires C = 67.42; H = 5.62 per cent.

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The density determinations gave:

$$d 58^{\circ}/4^{\circ} = 1.1663$$
; $d 74.7^{\circ}/4^{\circ} = 1.1495$; $d 99.8^{\circ}/4^{\circ} = 1.1264$; $d 124^{\circ}/4^{\circ} = 1.1041$.

and the following polarimetric observations were made :-

Rotation of methylic dimetatoluylglycerate.

Temperature.	Observed rotation, an, in 49.92 mm. tube. +15.88°	d t°/4°. 1·2030	[ø] _{D.} + 26·44°
51	+13.11	1.1728	+ 22.39
73 ·5	+11.20	1.1510	+19.49
98.2	+9.31	1.1280	+16.54
109	+8.53	1.1178	+15.29
138	+6.27	1.0903	+11.53

Ethylic Dimetatoluylglycerate (Active).

The preparation was similar to that of the methylic compound, and, ike the latter, it could not be induced to crystallise.

I.
$$0.2073$$
 gave 0.5171 CO₂ and 0.1089 H₂O. C=68.03; H=5.83.
II. 0.2053 , 0.5125 CO₂ , 0.1081 H₂O. C=68.08; H=5.85.
C₂₁H₂₂O₆ requires C=68.11; H=5.95 per cent.

The density determinations gave:

$$d \ 56^{\circ}/4^{\circ} = 1.1436$$
; $d \ 70.8^{\circ}/4^{\circ} = 1.1300$; $d \ 98.4^{\circ}/4^{\circ} = 1.1060$; $d \ 124^{\circ}/4^{\circ} = 1.0833$,

and the following polarimetric observations were made:-

Rotation of ethylic dimetatoluylglycerate.

	Observed rotation, an,			
Temperature.	in 49 92 mm. tube.	$d t^{\circ}/4^{\circ}$.	•	[a] _{D.}
18·5°	+ 15·90°	1.1770		+ 27·06°
52·5	+13.25	1.1466		+23.14
77.5	+11.25	1.1243		+20.04
99·1	+9.68	1.1050		+17.55
109	+8.73	1.0960		+ 15.95
138	+6.40	1.0705		+11.98

Methylic Diorthotoluylglycerate (Active).

The mode of preparation was similar to that adopted in the case of the meta-compound. It was only obtainable as an oil possessing a slight yellow colour, which boiling in alcoholic solution with animal charcoal failed to remove.

I. 0·2000 gave 0·4937 CO₂ and 0·0993 H₂O. $C = 67 \cdot 32$; $H = 5 \cdot 51$. II. 0·2024 ,, 0·4993 CO₂ ,, 0·1014 H₂O. $C = 67 \cdot 28$; $H = 5 \cdot 56$. $C_{20}H_{20}O_6$ requires $C = 67 \cdot 42$; $H = 5 \cdot 62$ per cent.

The density determinations gave:

$$d 58\cdot2^{\circ}/4^{\circ} = 1\cdot1773$$
; $d 72^{\circ}/4^{\circ} = 1\cdot1659$; $d 98^{\circ}/4^{\circ} = 1\cdot1404$;
 $d 128\cdot7^{\circ}/4^{\circ} = 1\cdot1107$.

and the following polarimetric observations were made:-

Rotation of methylic diorthotoluylglycerate.

	Observed rotation, a D,		
Temperature.	in 49 92 mm. tube.	$d t^{\circ}/4^{\circ}$.	[α] _{D.}
20°	+ 12·23°	1.2135	+ 20·19°
49	+10.45	1.1865	+17.64
76	+8.90	1.1610	. +15.36
98.5	+7.50	1.1390	+13.19
109	+6.98	1.1295	+12.39
139	+5.28	1.1010	+9.61

Ethylic Diorthotoluylglycerate (Active).

This was prepared in the same way as the meta-compound, and, like it, could only be obtained as a nearly colourless oil.

I. 0.2000 gave 0.4995
$$CO_2$$
 and 0.1037 H_2O . $C = 68.11$; $H = 5.76$. II. 0.2095 , 0.5230 CO_2 , 0.1112 H_2O . $C = 68.08$; $H = 5.90$. $C_{21}H_{22}O_6$ requires $C = 68.11$; $H = 5.95$ per cent.

The density determinations gave:

$$d 61^{\circ}/4^{\circ} = 1.1562$$
; $d 77^{\circ}/4^{\circ} = 1.1421$; $d 98.7^{\circ}/4^{\circ} = 1.1217$; $d 123.9^{\circ}/4^{\circ} = 1.0973$; $d 134^{\circ}/4^{\circ} = 1.0888$,

and the following polarimetric observations were made: --

Rotation of ethylic diorthotoluylglycerate.

Temperature.	Observed rotation, an, in 49.92 mm. tube.	d t°/4°.	[a] _D .
19·5°	+12·93°	1 1940	+21.69°
50	+10.77	1.1663	+ 18.51
81	+8.91	1.1379	+15.69
98	+7.83	1.1214	+13.98
109.5	+7.18	1.1110	+12.94
140	+5.30	1.0817	+9.81

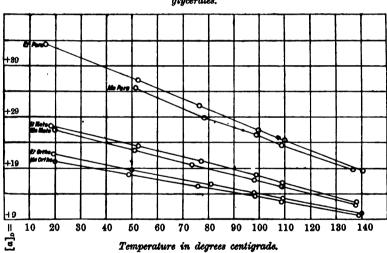
A comparison between these values and those previously obtained by one of us (Trans., 1896, 69, 106 and 108) for methylic dibenzoyl-

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glycerate and ethylic dibenzoylglycerate respectively shows that, not only are the rotatory powers of the dibenzoylglycerates almost identical, but that they also very closely approximate to those of the corresponding metatoluylglycerates.

Comparison of the Rotatory Powers of the Ditoluylglycerates.

The comparative rotatory powers of the compounds under consideration are rendered most apparent by means of the accompanying diagram, from which it will be seen that, in the case of the isomeric ditoluyl-glycerates, the para-compound has markedly the highest, and the ortho-compound the lowest, dextrorotation. The specific rotations of the isomeric toluyl compounds tend to approximate at high temperatures.



Specific rotations of methylic and ethylic ortho-, meta-, and para-ditoluylglycerates.

In the case of the toluyl compounds, the ethylic salt has invariably a higher dextrorotation than the methylic, but the difference is not very great and tends to disappear at high temperatures.

Attention has previously been called (loc. cit.) to the fact that methylic and ethylic dibenzoylglycerate are of almost identical specific rotation, but over the common range of temperatures, at which observations were made, the dextrorotation of the ethylic is somewhat in excess of that of the methylic salt. The approximation between the rotatory powers of the methylic and ethylic salts of the ditoluylglycerates is nearly, but not quite, as pronounced as in the case of the dibenzoylglycerates.

Methylic and ethylic dibenzoylglycerate have not been included

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on the accompanying diagram, as their curves are so nearly coincident, not only with each other, but also with those of the metatoluylgly-cerates, that their introduction would only have led to confusion.

The relationship between the rotations of the several compounds in question is also exhibited by means of the following comparisons made at 20° and at 100° respectively:—

	[a] _D ^{20°}	[a] ^{100°}
Methylic diparatoluylglycerate	+41 [.] 21°	+ 25 ·09°
Ethylic ,,		+26.18
Methylic dibenzoylglycerate	+ 26.67	+17.43
Ethylic ,,	+ 26.08	+18.05
Methylic dimetatoluylglycerate	+26.40	+16.45
Ethylic ,,	+ 26.89	+17.40
Methylic diorthotoluylglycerate	+ 20.19	+13.08
Ethylic ,,	+ 21.64	+13.80

Molecular Volumes.

The following are the molecular volumes, both experimental and calculated according to Traube's formula, of the compounds in question:—

						Wolecniar Adinme at 19		
						Ex	perimental.	Calculated.
Methylic di	benzoylglycerate		$\frac{\text{Mol. wt.}}{d \ 15^{\circ}/4^{\circ}}$	=	$\frac{328}{1\cdot2211}$	=	268.6	260.3
Ethylic	,,	•••	"		$\frac{342}{1.2010}$	=	284.8	276.4
Methylic di	iparatoluylglycer	ate.	"		$\frac{856}{1\cdot2025}$	=	296 0	292.5
Ethylic		•	,,		$\frac{370}{1\cdot 1698}$	=	316.3	808.6
Methylic di	imetatoluylglycer	ate.	"		356 1·2093	=	294.4	292.5
Ethylic	,,		,,		$\frac{870}{1.1813}$	=	313.2	808.6
Methylic d	iorthotoluylglyce	rate	,,		356 1·2130	=	293.5	292.5
Ethylic	"	•	,,		370 1·1967	=	809.2	808.6

From the above table, it will be seen that, in the case of the isomeric ditoluylglycerates, the para-compound has the largest and the orthocompound the smallest molecular volume, and that the rotations, therefore, stand in the same sequence as the molecular volumes. A similar relationship has been already shown by one of us to generally hold good in the case of other active ortho-, meta-, and para-compounds previously investigated.

Again, it will be seen that all the experimental molecular volumes are in excess of those calculated by Traube's formula, but that whilst the experimental molecular volumes of the ortho-compounds approximate very closely to the calculated ones, the divergence is marked in the case of the meta-, and still more considerable in that the paracompounds.

In the case of the dibenzoylglycerates, the experimental are even still more in excess of the calculated values than in the case of the diparatoluylglycerates.

Thus, although the relationship between the experimental and calculated molecular volumes does not afford direct evidence of association in the case of any of these compounds, it is obvious that the values calculated by Traube's formula must not be interpreted too rigidly, and that possibly some association may exist notwithstanding.

Rotation in Solution.

It appeared of interest to ascertain whether the relation between the rotatory power of the methylic and ethylic compounds is maintained in solution, and we have therefore determined the rotation of methylic and ethylic diparatoluylglycerates dissolved both in alcohol and in acetone. The results, which are given below, show that in these

Weight of solution. Grams.	Weight of substance. Grams.	Grams substance in 100 grams solution.	Density of solution at temp. of observation of rotation.	Temp. of observation	Observed rotation, a _D , in 299.84 mm. tube.	[a] _D .	
Ме	thylic dipo	vratoluylg	lycerate in	ethylic al	cohol solut	ion.	
21.0000	1.0000	4.7619	0.8078	20°	+ 4·53°	+89.80°	
	Methylic	diparatolu	ylglycerate	in aceton	e solution.		
21.0000	1.0000	4.7619	0.8068	20°	+4·02°	+84·92°	
	[Rotation i	n liquid sta	te; $[a]_{D}^{20^{\circ}} =$	+41.21° (ca	lculated.)]		
Et	hyl i c dipa	ratoluylgl	ycerate in	ethylic alc	ohol soluti	on.	
21.0000	1.0000	4.7619	0.8081	20°	+4·80°	+41.60°	
	Ethylic diparatoluylglycerate in acetone solution.						
21 .0000	1.0000	4.7619	0.8065	20°	+4·22°	+86.65°	
'	[Rotation i	n liquid sta	te; $[\alpha]_{D}^{20^{\circ}} =$	+ 42·41° (ca	lculated.)]	•	

solvents also the ethylic has a somewhat higher dextrorotation than the methylic compound. The rotations are higher in alcohol than in acetone solution, but even in the former solvent are somewhat less than those of the pure substances at the same temperature. Thus, if these solvents effect any breaking down of association amongst the molecules, this process is attended with a diminution, and not an increase, in the rotatory power. The effect of these and other solvents on the rotatory power and molecular weight of these compounds is at present being further investigated by one of us.

In conclusion, we would express our indebtedness to the Government Research Fund for assistance in carrying out this investigation.

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XLVIII.—Isomeric Fencholenic Acids.

By GEORGE BERTRAM COCKBURN, B.A., B.Sc.

That a striking analogy exists between camphor and fenchone in many of their compounds has been previously shown by Wallach (Annalon, 1890, 259, 325; 1892, 269, 332; 1894, 284, 324; 1898, 300, 294), and by Gardner and the author (Trans., 1897, 71, 173; 1898, 73, 275, 704, 708). One of the characteristic points in common is the behaviour of the oximes of these substances; unlike most cyclic oximes, they do not regenerate the original ketone on boiling with dilute acids, but, on the contrary, lose water and pass to an unsaturated nitrile, which gives an unsaturated acid on hydrolysis. The unsaturated acid, C_9H_{15} :COOH, isomeric with campholenic acid, which Wallach obtained from fenchonoxime, is known as fencholenic acid, and attention was drawn by this chemist to the fact that, whilst two isomerides were known in the case of campholenic acid, only one acid was obtained from fenchone.

On repeating Wallach's work, it was found that, on hydrolysing the nitrile, the product does not consist, as he states, merely of a mixture of the amide, which is difficult to hydrolyse, and of liquid fencholenic acid, but that a third substance is present in the acid portion of the mixture. This is an isomeride of the liquid acid, and, unlike the latter, is readily crystalline.

It seems probable that Wallach's liquid acid was really a mixture of the solid (β -) and the liquid (α -) acids, as the melting point of the amide which he obtained by heating the ammonium salt is far too low for the amide of the liquid acid—a point on which he him-

self comments. Further, the amides, when not mixed with one another, are very easily purified, a fact which suggests that he was dealing with a mixture of the two acids. Any portion of the acid which he obtained by hydrolysing the amide produced in the first operation would be pure and unmixed with the β -acid, as the amide of the latter hydrolyses with as great ease as the former does with difficulty, and would consequently be wholly converted into acid in the first operation.

Wallach's observations on the boiling point of the nitrile also tend to prove that he was working with a mixture; his specimen boiled at $217-218^{\circ}$, whereas the experimental work in the present paper shows that the pure nitrile of the liquid acid boils at $211-212^{\circ}$, and that of the solid acid at $217-219^{\circ}$. The mixture of the nitriles produced by the action of dilute sulphuric acid on the oxime boils between 214° and 219° ; the greater portion, passing over at $217-218^{\circ}$, yields 50-60 per cent. of the β -acid.

According to Wallach, the salts of fencholenic acid with the alkalis and alkaline earths do not crystallise, and are ill-defined. This is true in the main of the liquid acid, as the calcium and magnesium salts can be obtained crystalline, but only with difficulty; in the case of the solid acid, however, the salts of the alkaline earths are readily crystallisable, although those of sodium and potassium are not. The failure of salts of the liquid acid to crystallise appears to be due to the action of water, as the calcium salt after boiling with water no longer crystallises but turns into a sticky paste, an effect which does not appear to be due to any chemical change, for when liberated from this salt the acid boils at the same temperature as before.

The solid fencholenic acid is much more stable towards halogen hydrides than the liquid isomeride; the latter readily combines with hydrogen chloride and hydrogen bromide, forming crystalline compounds, but corresponding compounds from the solid acid have not yet been obtained, and it resists almost entirely the action of hydrogen bromide at 100°. With bromine, the solid acid forms a liquid and a solid compound; the latter is a monohydrobromide, and owes its origin to the considerable amount of hydrogen bromide given off during the absorption of the bromine, but whether it is produced by elimination of hydrogen bromide from the dibromide at first formed, or by direct addition of hydrogen bromide, is not clear, although the former seems more probable.

Fenchone consequently corresponds exactly to camphor in giving an oxime which does not regenerate the original ketone by the action of dilute acids, but, losing a molecule of water in two different ways, produces two isomeric unsaturated acids corresponding to α - and β -campholenic acids. The liquid fencholenic acid I have designated as the

 α - and the solid as the β -acid, in order to correspond to the liquid and solid campholenic acids.

It may be mentioned that no interconversion between the α - and β -acids, such as is found in the campholenic series, has been observed in the case of the fencholenic acids.

The preparation of fencholenic acid was undertaken with the object of studying its oxidation products to see in what way they agreed with the interesting series of compounds obtained from the two campholenic and pinonic acids. This work is at present under investigation.

EXPERIMENTAL.

Fenchonoxime was prepared from fenchone ($[a]_D + 61.9^\circ$) by Rimini's method (*Gazzetta*, 1896, 26, ii, 502), for, although this method is somewhat extravagant in the amount of hydroxylamine required, the yield is quantitative, whereas the product obtained by Wallach's method invariably contains some unchanged fenchone, and the yield rarely exceeds 70 per cent. of the theoretical.

The conversion of oxime to nitrile was effected as follows. Fenchonoxime (50 grams) is added to a mixture of 250 c.c. water and 10 c.c. sulphuric acid; on warming, it partially dissolves, but after boiling, separates as a liquid layer on the surface of the water. The boiling is continued for an hour, the contents of the flask are then cooled, the upper layer separated, and the liquid extracted with ether; the nitrile present in the upper layer and in the ethereal extract is then distilled. It boils at 214—219°, and not at 217—218° as Wallach states.

β-Fencholenic Acid.

The nitrile is hydrolysed by heating with alcoholic potash as described by Wallach (Annalen, 1892, 269, 332). After heating for 7 days, the alcohol is removed by distillation in a current of steam, the contents of the distilling flask are diluted with water, and the a-amide, which separates, is filtered off. The aqueous solution is evaporated until two layers separate; the upper layer, consisting of potassium fencholenate, is removed, diluted with water, and thoroughly extracted with ether. On acidification, an oily layer rises to the surface, and after removing this, the liquid is extracted with ether, and the ethereal extract added to the oil previously separated. In the course of 24 hours, crystallisation occurs to a considerable extent, and further crops of crystals are subsequently obtained; when the last crop has been formed by keeping the oil freed from ether at 0° for a long time, there still remains in the oily residue about 10 per cent. of the solid acid, which can only be removed by careful fractionation of the oil in a vacuum, and afterwards placing the portions of higher boiling

point in a freezing mixture. In this way, the liquid acid can be obtained practically pure. Subsequent investigation of the a- and β -nitriles showed that the best separation of the two acids is effected by allowing the hydrolysis to proceed for $2\frac{1}{2}$ instead of 7 days. The whole of the β -nitrile is then converted to acid, whilst only a small quantity of a-acid is formed, owing to the difficulty with which the a-amide is hydrolysed. The a-amide can then be separately used for the preparation of the a-acid. The yield of β -acid by this method is from 55 to 60 per cent., and of a-amide 35 per cent. of the theoretical, the remainder being a-acid.

β-Fencholenic acid may be easily purified by crystallisation from light petroleum; it melts at 72—73°, boils without decomposition at 140.5—141.5° under 12 mm. pressure, and at 259—260° under the ordinary pressure, and has the specific rotatory power $[a]_D + 19.64$ ° in alcoholic solution.

0.2200 gave 0.5755 CO₂ and 0.1898 H₂O. C=71.41; H=9.58. C_9H_{15} .COOH requires C=71.43; H=9.52 per cent.

It is readily soluble in alcohol, ether, ethylic acetate, and acetone; less so in benzene and glacial acetic acid, and crystallises well from these; it is fairly soluble in hot, but only slightly so in cold light petroleum, and crystallises from it in fine, large plates from 2 to 2.5 cm. in length. It immediately decolorises bromine and permanganate solutions, and from its method of formation is undoubtedly unsaturated.

The sodium and potassium salts cannot be obtained crystalline; on evaporating their solutions, an oil is formed which eventually becomes semi-solid, and similar results are obtained on adding ether to the alcoholic solution of the salts.

The ammonium salt is formed on passing ammonia into a dry ethereal solution of the acid. It is a white powder which is not very stable, losing all its ammonia at 100°, and reproducing fencholenic acid. When heated at higher temperatures in a sealed tube, it gives the corresponding amide.

The salts of the alkaline earths are well defined and crystallise readily, differing in this respect from the corresponding a-salts.

Calcium β -fencholenate, $(C_{10}H_{15}O_2)_2Ca + 3H_2O$, formed by neutralising an alcoholic solution of the acid with lime water, crystallises in small needles which are readily soluble in warm water or alcohol, but only moderately so in the cold.

0.2144 gave 0.0273 H_2O and 0.0275 CaO. $H_2O=12.73$; Ca=9.16. $(C_{10}H_{15}O_2)_2Ca+3H_2O$ requires $H_2O=12.61$; Ca=9.34 per cent.

The barium salt, $(C_{10}H_{16}O_2)_2Ba + 7H_2O$, crystallises in well defined plates, and is less soluble than the calcium salt.

The magnesium salt, obtained by adding a fairly concentrated solution of magnesium sulphate to a solution of sodium β -fencholenate, crystallises with $7 \, \mathrm{H}_2\mathrm{O}$, and is much less soluble than the calcium or barium salts.

The copper salt separates in shiny green scales, slightly soluble in water; on analysis by ignition in hydrogen:

0.3215 gave 0.0513 Cu. Cu = 15.95. $(C_{10}H_{15}O_{2})_{2}$ Cu requires 15.9 per cent.

The zinc, ferric, lead, and mercuric salts are precipitated on adding the corresponding chlorides to a neutral solution of the acid.

β-Fencholenamids.—In the very considerable amount of amide formed in the hydrolysis of the nitrile obtained from the oxime, only one substance, that described by Wallach as melting at 113—114°, can be found. The question whether this was the origin of the solid acid was settled by preparing the ammonium salt of the latter and heating it in a sealed tube at 180° for 5 hours; at this temperature, only a small amount of charring occurred, and on crystallising the contents of the tube from light petroleum and alcohol, the amide melted at 86.5—87.5°. It was readily soluble in ether and alcohol, but in light petroleum it dissolved only slightly when warm, and was practically insoluble when cold; it crystallised in soft, silky needles.

0.1989 gave 15.32 c.c. nitrogen at 18.5° and 739 mm. N=8.59. $C_9H_{15}\cdot CONH_2$ requires N=8.38 per cent.

a- and β -Fencholenic Nitriles.

On warming the β -amide with phosphorus pentoxide on the oil-bath at 60°, it passes readily to the corresponding nitrile, which is purified by pouring into water and distilling in steam. The β -nitrile is a clear, colourless liquid with a specific gravity of 0.9203 at 15.6°, and a specific rotatory power of $[a]_{\rm D}+43.66^{\circ}$ in alcoholic solution; it boils at 217—219°, and appears at first sight to be identical with Wallach's nitrile (b. p. 217—218°). This, however, is not the case, since both the nitrile and its corresponding amide pass quantitatively and with the greatest ease to β -fencholenic acid on hydrolysis, the time required being only about one-tenth of that necessary for the conversion of the a-amide to its acid.

To compare the α - and β -nitriles, the former was prepared by a similar method to that employed for the latter from the amide melting at 113—114°. In this case, the action is not so rapid, and a higher temperature being required, a certain amount of decomposition takes place. The α -nitrile was purified as before, and boiled constantly at 211—212°; its specific gravity was 0.9136 at 15.6°, and the

specific rotatory power was $[a]_D + 28.98^\circ$ in alcoholic solution. On boiling with alcoholic potash, this nitrile is readily converted into the amide melting at 113—114°, but only with difficulty into the liquid acid; 30 grams of nitrile, after 14 days boiling, give 14—15 grams of the latter.

In the production of the two nitriles from the oxime, it was thought that the strength of the acid might be an important factor in the formation of the two acids. Investigations were consequently made with 4, 8, 16, and 32 per cent. sulphuric acid, but in no case was any marked difference observed. Variation in the length of time during which the boiling was continued also had no effect on the yield.

Action of Halogens on a- and B-Fencholenic Acids.

Both acids decolorise bromine on the addition of the latter to their solutions in light petroleum, cooled in a freezing mixture. During the action, a considerable amount of hydrogen bromide is evolved in each case. After evaporation of the petroleum, the solid acid gives a crystalline compound and a thick, black oil; the former may be easily obtained pure by means of light petroleum, in which it is not very soluble. It crystallises in long, thin needles, melts at $80-81^{\circ}$ without decomposition, and is insoluble in caustic soda solution. Analysis shows it to be formed by the addition of the elements of hydrogen bromide to fencholenic acid.

0.1921 gave 0.1452 AgBr. Br = 32.23. $C_{10}H_{17}O_{2}Br$ requires Br = 32.13 per cent.

Towards hydrobromic acid, solid fencholenic acid is very stable. Whilst the liquid acid combines with it when left at ordinary temperatures, the solid acid does not form an addition product, either in the cold or on heating in a sealed tube with acetic and hydrobromic acids at 100°, and in the latter case is for the most part recovered unchanged, mixed with a small amount of oil which contains only a very small percentage of bromine. The hydrobromide of the liquid acid melts at 96—100°, and is difficult to obtain pure, as it decomposes and liquefies in the air. The hydrochloride melts, as Wallach states, at 97—98°.

a-Fencholenic Acid.

a-Fencholenic acid is obtained pure by hydrolysing the amide melting at 113—114°, and distilling the acid thus produced. It is a thick, colourless oil boiling at 136—138° under 12 mm. pressure, and at 254—256° under ordinary pressure, with a slight amount of decomposition. It is heavier than, and insoluble in, water; the specific

gravity is 1.0069 at 16°, the specific rotatory power is $[a]_D + 30.73$ (not in solution).

0.2168 gave 0.5661 CO₂ and 0.1846 H₂O. C = 71.21; H = 9.46. C_9H_{15} ·COOH requires C = 71.43; H = 9.52 per cent.

According to Wallach, the salts of this acid do not crystallise. The calcium salt, $(C_{10}H_{15}CO_2)_2Ca+4H_2O$, however, may be obtained crystalline by neutralising a solution of the acid in alcohol with lime water, and then rapidly evaporating the solution by heating in a vacuum. The crystalline salt was filtered, dried, and analysed, the water being determined at 80° , as decomposition ensues at 100° .

0.3227 gave 0.0512 H_2O and 0.0412 CaO. $H_2O = 15.87$; Ca = 9.11. $(C_{10}H_{15}CO_2)_2Ca + 4H_2O$ requires $H_2O = 16.14$; Ca = 8.97 per cent.

Prolonged contact with water, or boiling with water, turns the crystalline salt into a gummy mass which resists all attempts at crystallisation.

The magnesium salt is obtained in the same way as that of the β -acid, but is very sensitive to the action of water, and cannot be obtained sufficiently well-defined for analysis.

XLIX.—Synthesis of some Derivatives of \$\beta\$-Dipyridyl from Citrazinic Acid.

By W. J. SELL, M.A., F.I.C., and H. JACKSON, B.A., B.Sc.

Ir has been shown (Sell and Easterfield, Trans., 1893, 63, 1036) that when citrazinic acid is treated with nitrous fumes, several interesting substances are produced, which are either themselves coloured or readily produce coloured derivatives. At that time, little more than an analysis and a short description of each was attempted. The substances are non-volatile, practically insoluble in such cold menstrua as are readily available for freezing point determinations, and beyond a few indications from chemical sources, no information as to their molecular weight was easily obtainable. The publication last year, however, by Walker and Lumsden (Trans., 1898, 73, 502) of a convenient modification of Landsberger's boiling point method made it possible to determine the molecular weights of several of these compounds. The present paper deals with the work done in this direction. the deductions that may be made from the results obtained, and inci dentally describes the new compounds isolated during its progress.

When nitrous fumes, evolved from arsenious oxide, are passed through a magma of citrazinic acid and water until the greater part of the acid has dissolved, crystals are deposited, after filtration and standing, which may be recrystallised from hot acetone or alcohol. Analysis and a molecular weight determination point to the formula C.H.N.O. + H.O for this substance. With acetyl chloride, it gives a monacetyl derivative, and with phenol and sulphuric acid the usual colour reactions characteristic of nitroso-derivatives. regarded as nitrosocitrazinic acid, provisionally described (loc. cit.) as isonitrosocitrazinic acid, and the isomeric substance, formed from citrazinic acid by the action of nitric oxide in presence of air, as the isonitroso-derivative or oxime. The latter, which gives no colour reaction when Liebermann's test is applied, will be dealt with in a subsequent paper. The formation of the nitroso-derivative may be explained as follows:

Citrazinic acid. Nitrosocitrazinic acid.

When nitrosocitrazinic acid is oxidised with nitrous or nitric acid, an acid is formed crystallising in golden-yellow needles, which, on analysis, were found to have a composition agreeing with that required for the formula $C_6H_2N_2O_5 + 4H_2O$. As, however, a molecular weight determination indicates that this formula must be doubled, the compound would appear to be formed by the oxidation of two molecules of the nitroso-acid which become associated forming a dipyridyl derivative, as shown in the formulæ:

The yellow acid still retains the nitroso-groups, giving Liebermann's test with facility, and although, like nitrosocitrazinic acid, it explodes when heated, it is much more stable than the latter in acid solutions. With hydroxylamine hydrochloride, it gives a fine hydroxylamine salt, but no oxime has thus far been obtained. The acid is reduced by gently heating with stannous chloride, carbon dioxide being freely evolved, and after removal of the tin by hydrogen sulphide and exposure of the solution to the air, a beautiful crystalline substance having a bronze-green appearance is deposited. Analysis of this compound leads to the formula $C_5H_3NO_3$ being assigned to it. The same substance is also produced from nitrosocitrazinic acid by boiling with dilute sulphuric acid (*loc. cit.*), or from citrazinic acid by warming with a nitrite.

Attempts to determine its molecular weight were unsuccessful, owing to its sparing solubility, but it would seem to be a $\beta\beta$ -dipyridyl derivative, for (1) when boiled with fuming hydriodic acid and phosphorus it readily yields aa'-diglutaric acid (Trans., 1894, 65, 830), the molecular weight of which has been determined; (2) it is formed from the yellow acid mentioned above, and (3) chlorosulphonic acid at 100° converts it into a substance having a molecular weight which corresponds to that of a dipyridyl derivative. When boiled with benzoyl chloride, the substance gives a tetrabenzoyl derivative. These facts lead to the conclusion that it is a tetrahydroxydioxy- $\beta\beta$ -dipyridyl, and that in the passage from the yellow acid to the bronze-green compound the nitroso-groups are replaced by hydroxyl, and at the same time the carboxyl groups lose carbon dioxide. In reality, the action of a slight excess of stannous chloride is not quite so simple, as it converts the yellow acid into the colourless hexahydroxyl derivative, and this, after the removal of the tin, is oxidised by atmospheric oxygen, turning blue, and depositing the tetrahydroxydioxy-compound thus:

Dinitrosodihydroxydioxy-86'-dipyridyldicarboxylic acid.

Bronze-green compound. Tetrahydroxydioxy-\$\beta'-dipyridyl.

A very interesting reaction occurs when this bronze-green compound is boiled with hydriodic acid and a little ordinary phosphorus. An acid is produced (loc. cit.) which, on analysis, is found to have the formula $C_5H_7O_4$, but does not correspond to any acid hitherto isolated. Moreover, the molecular weight determination shows that its true formula is double this. It is a strong tetrabasic acid, and we assume it to be aa'-diglutaric acid. The subjoined formulæ show the nature of the change, the nitrogen being split off as ammonia:

Now it has been shown by Hofmann (Ber., 1883, 16, 590) that pyridine is converted by hydriodic acid into normal pentane and ammonia, thus:

Further, Weidel (Monats., 1891, 11,502) showed that the monocarboxylic acids and certain dicarboxylic acids of pyridine yield fatty acids when reduced, and that, in particular, nicotinic acid gave a-methylglutaric acid and ammonia, thus:

A similar result was obtained by Guthzeit and Dressel (Annalen, 1891, 262, 89) by the reduction of ethylic hydrogen ethoxyhydroxypyridinedicarboxylate by means of tin and hydrochloric acid, glutaric acid being formed:

The last two cases partake partly of a reducing and partly of an oxidising character, water being decomposed in the process. Of an entirely oxidising character is the formation of glutaric acid from piperidine by such a reagent as hydrogen dioxide, thus:

$$\begin{array}{cccc} \operatorname{CH}_2 & & \operatorname{CH}_2 \\ \operatorname{CH}_2 & \operatorname{CH}_2 & \rightarrow & & \operatorname{CH}_2 \\ \operatorname{CH}_2 & \operatorname{CH}_2 & & \rightarrow & & \operatorname{COOH} & \operatorname{COOH} \end{array}$$

If, then, pyridine or its derivatives, by the action of reducing agents, can give rise in many cases to either normal pentane or its di-

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basic or substituted dibasic acid—glutaric acid—then dipyridyl may be expected, under similar circumstances, to give dipentane or its tetrabasic acid, the particular compound formed, of course, being dependent on the dipyridyl reduced, the agent employed, and the temperature at which the reduction takes place. The effect of this last condition is especially noticeable when hydriodic acid is used. In the case under consideration, the reduction was effected under ordinary atmospheric pressure, and if, as has been shown, the pyridine rings are linked through the $\beta\beta'$ -positions to form $\beta\beta'$ - (or 3:3'-) oxydipyridyl, then the acid produced by the action of hydriodic acid and phosphorus would be $a\alpha'$ -diglutaric acid.

If, however, the bronze-green substance is covered with fuming hydriodic acid and the mixture left for some hours, practically colourless crystals having the composition (C₁₀H₂N₂O₆+H₂O)2HI may be isolated (Trans., 1894, 65, 830), which, when decomposed by water, yield the base C₁₀H₂N₂O₆+H₂O, in yellowish-white needles. This substance, previously described under the name of hydroquinoketopyridine, is hexahydroxy- $\beta\beta$ -dipyridyl. It has since been discovered that a more ready method for the isolation of this substance is the reduction of the bronze-green compound by means of tin and hydrochloric acid. The bronze-green compound is converted into a mass of faintly coloured needles of the hydrochloride of the hexahydroxyderivative, from which hydrogen chloride is removed by decomposition with water, leaving the nearly white, crystalline base. when heated with benzoyl chloride, gives the hexabenzoyl derivative, thus showing that the compound contains six hydroxyl groups. reconverted into the tetrahydroxydioxy-derivative by such gentle oxidising agents as ferric chloride.

On oxidation with nitric acid, the bronze-green compound is almost quantitatively converted into a golden-yellow substance, which can be easily recrystallised from hydrochloric acid. Analysis led to the formula $C_5H_2NO_3$ being assigned to it. No suitable solvent could be found for a molecular weight determination. It is reduced to the bronze-green compound by such reducing agents as sulphurous acid or quinol. The same result takes place when its solution is mixed with that of the hexahydroxy-derivative, the compound separating in magnificent needles. With hydroxylamine hydrochloride, the solution in strong hydrochloric acid gives an oxime, $C_5H_2NO_2:N\cdot OH$, which is blood-red in colour; it also gives, under the same conditions, a semicarbazone, $C_5H_2NO_2:N\cdot NH\cdot CO\cdot NH_2$, crystallising in greenish-yellow needles.

The preparation of this substance from the bronze-green derivative may be sketched as follows:

A substance of this composition would be a dihydroxydiparaquinone of $\beta\beta$ -dipyridyl, and should, of course, give a tetroxime instead of a dioxime. It must, however, be borne in mind that the only condition at present found for their preparation involves the use of concentrated hydrochloric acid, and is not an ideal one for the preparation of all possible oximes.

It is not without interest to compare the substances considered above with some oxy-derivatives obtained from diphenyl, the analogue of dipyridyl in the benzene series. We have, for example, hexahydroxydiphenyl, the parent substance of cœrulignone or cedriret, which is strictly analogous to hexahydroxydipyridyl, thus:

$$\begin{array}{ccc} C_6H_2!(OH)_8 & C_5HN!(OH)_8 \\ C_6H_2!(OH)_8 & C_5HN!(OH)_8 \\ \text{Hexahydroxydiphenyl.} & \text{Hexahydroxydipyridy} \end{array}$$

Again, corrulignone has the constitution represented by formula I, and its relation to the dioxytetrahydroxy- $\beta\beta$ '-dipyridyl, frequently described above, for brevity's sake, as the bronze-green derivative, is shown by the formulæ:

$$\begin{array}{lll} \text{O}\cdot \text{C}_6\text{H}_2\text{:}(\text{OCH}_3)_2 & \text{O}\cdot \text{C}_6\text{H}_2\text{:}(\text{OH})_2 & \text{O}\cdot \text{C}_5\text{HN:}(\text{OH})_2 \\ \text{O}\cdot \text{C}_6\text{H}_2\text{:}(\text{OCH}_8)_2 & \text{O}\cdot \text{C}_6\text{H}_2\text{:}(\text{OH})_2 & \text{O}\cdot \text{C}_5\text{HN:}(\text{OH})_2 \\ \text{I.} & \text{II.} & \text{III.} \\ \text{Corrulignone.} & \text{Bronze-green substance} \end{array}$$

These substances are highly coloured and form blue solutions in various menstrua. It is intended to attempt the preparation of tetramethoxydioxy- $\beta\beta'$ -dipyridyl at an early date.

The action of chlorosulphonic acid on the bronze-green substance is most remarkable; a somewhat violent reaction occurs, and from the product a white substance crystallising from glacial acetic acid in fine colourless needles may be isolated. Analysis points to the formula $C_{10}H_4Cl_2N_2O_8$, and the molecular weight determinations agree with this formula. With benzoyl chloride, it gives the derivative $C_{10}H_2N_2Cl_2O_8(CO\cdot C_6H_5)_2$, and also forms a sodium salt having the composition $C_{10}H_2Cl_2N_2O_8Na_2+3H_2O$. These facts show that the substance has two hydroxyl groups. It may be looked upon as derived from the tetrahydroxydioxy- $\beta\beta$ '-dipyridyl by the replacement of two hydroxyl groups by chlorine, whilst at the same time an atom of oxygen has been removed. The subjoined formulæ explain the nature of the change:

In this case, the compound formed would find its analogue in a derivative of diphenylene oxide thus:

These formulæ clearly show the analogy which exists, the CH-group in diphenylene being replaced by an atom of nitrogen in the new compound.

The authors are well aware that in some cases the formulæ employed in this paper are open to criticism; they represent their views, however, at the present time.

EXPEBIMENTAL. COOH β -Nitrosocitrazinic Acid, $\stackrel{\text{NO}}{\text{OH}} \stackrel{\text{H}}{\underset{\text{N}}{\text{O}}}$.

The preparation of this substance by the action of nitrous fumes on a magma of the acid and water has been described (Trans., 1893, 63, 1046). Analysis showed its formula to be $C_6H_4N_2O_5+H_2O$, and it was regarded as the isonitroso-derivative.

Determination of Molecular Weight.—This was carried out by determining the elevation of the boiling point of absolute alcohol when a known weight of the dry substance is dissolved in that solvent; the modification of Landsberger's apparatus devised by Walker and Lumsden (Trans., 1898, 73, 502) being used throughout this investigation of molecular weights.

(I.)
$$0.3070$$
 gram in 18 c.c. alcohol gave 0.325° elevation. Mol. wt. = 185 . (II.) 0.3070 , 15 c.c. , 0.151° , Mol. wt. = 176 .

Theoretical value for $C_6H_4N_2O_5 = 184$.

This points to the substance having the simple formula given above.

Action of Acetyl Chloride on Nitrosocitrazinic Acid.—One gram of the acid was boiled with acetyl chloride and a few drops of acetic anhydride until complete solution was obtained. The filtered solution, on evaporation over solid caustic potash, gave greyish-white crystals,

which were drained on the filter pump, washed with acetyl chloride, and dried in a vacuum over caustic potash. The substance was extremely explosive, and was analysed after mixing with copper oxide in the boat.

0.1468 gave 0.2280 CO₂ and 0.036 H₂O.
$$C = 42.68$$
; $H = 2.71$. $C_6H_3N_2O_5(CO\cdot CH_8)$ requires $C = 42.85$; $H = 2.67$ per cent. $C_6H_2N_2O_5(CO\cdot CH_8)_2$, $C = 44.79$; $H = 3.1$,

This result points to the existence of one hydroxyl group in the substance as indicated by the formula. The attempts to prepare a benzoyl derivative were unsuccessful, owing to the instability of the original acid.

Dinitrosodihydroxydioxy-etaeta-dipyridyldicarboxylic Acid,

If nitrosocitrazinic acid is oxidised by means of nitrous or nitric acids, this substance, previously described as the yellow acid, $C_6H_2N_2O_5+4H_2O$ (loc. cit., 1050), is produced. The molecular weight, as found by noting the elevation of the boiling point of absolute alcohol, corresponds to the double of this.

0.695 dry acid in 15 c.c. alcohol gave
$$0.20^{\circ}$$
 elevation. Mol. wt. = 361. 1.03 ,, 16 c.c. ,, 0.29° ,, Mol. wt. = 346. Theoretical value for $(C_6H_2N_2O_5)_3 = 360$.

With hydroxylamine hydrochloride in excess, a crystalline precipitate is produced, consisting of golden-yellow needles. On analysis, it was found to be the hydroxylamine salt of the yellow acid, and is not the oxime, as was at first expected.

Tetrahydroxydioxy-
$$\beta\beta$$
-dipyridyl, OH
 N
 OH
 OH
 OH

If either nitrosocitrazinic acid or the yellow acid just described is reduced, a beautiful bronze-green compound is formed; this same substance is obtained by the action of potassium nitrite and a dilute

acid on citrazinic acid. On analysis, it is found to have the formula $C_5H_3NO_8+H_2O$. It is thus produced from the yellow acid by the removal of the carboxyl groups as carbon dioxide, as this gas can readily be detected during the preparation; the nitroso-groups are probably first replaced by oxygen, and, finally, the CO-groups are reduced to C(OH)-groups.

Action of Benzoyl Chlorids.—Two grams of the substance were boiled for half-an-hour with benzoyl chloride. The filtered solution was then allowed to remain over solid caustic potash in a vacuum desiccator for two days. There had then separated a mass of crystals which were drained on the pump, washed first with benzoyl chloride, finally with dry benzene, and then allowed to dry in a desiccator over paraffin, when they had the appearance of dark-brown, opaque plates.

```
0.1476 gave 0.3702 CO<sub>2</sub> and 0.0428 H<sub>2</sub>O. C = 68.39; H = 3.24. 0.1126 , 0.2821 CO<sub>2</sub> , 0.0325 H<sub>2</sub>O. C = 68.21; H = 3.21. C_{10}H_2N_2O_6(CO\cdot C_6H_5)_4 requires C = 68.67; H = 3.30 per cent.
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The analyses point to the existence of four hydroxyl groups in the substance as shown in the formula given. Attempts to determine its molecular weight were unsuccessful, owing to the sparing solubility of the substance in ordinary solvents.

It was shown (Trans., 1894, 65, 830) that when the bronze-green substance described above was boiled with fuming hydriodic acid and a little yellow phosphorus, there was obtained a beautiful, white, crystalline acid, which, on analysis, proved to have the formula $C_5H_7O_4$. The molecular weight of this substance was determined as in former cases.

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0.227 in 12 c.c. alcohol gave 0.125^{\circ} elevation. Mol. wt. = 237. 0.400 ,, 11 c.c. ,, ,, 0.225^{\circ} ,, Mol. wt. = 252. Theoretical value for (C_8H_7O_4)_2 = 258.
```

It is a strongly tetrabasic acid, and its mode of formation, together with its molecular weight, point to its being aa'-diglutaric acid.

Dimethylic Diglutarate.—If diglutaric acid is dissolved in excess of methylic alcohol, and dry hydrogen chloride passed in to saturation, the solution deposits a mass of fine, white needles when left in a vacuum desiccator over strong sulphuric acid. The substance was recrystallised from a small quantity of hot water, and finally dried in a vacuum. It melts sharply at 133°.

It is our intention to further examine the relationships of this interesting acid.

Dihydroxy-
$$\beta\beta$$
-dipyridyldiparaquinone, OH N O OH

When the bronze derivative is treated with nitric acid, it gives a golden-yellow substance of the formula $C_5H_2NO_2$. We believe it has the double ring formula, although all attempts to determine its molecular weight failed, owing to its being very sparingly soluble in such menstrua as are available for this purpose.

Dioxime.—The quinone is soluble in hot concentrated hydrochloric acid. To the cooled solution was added an excess of hydroxylamine hydrochloride dissolved in concentrated hydrochloric acid. After standing a few minutes, a beautiful, blood-red oxime separated; this was collected and repeatedly washed with water, and finally with a little ether. It was allowed to dry in the air, finally at 100°, and then analysed.

0.1548 gave 0.2465 $\rm CO_2$ and 0.0320 $\rm H_2O$. $\rm C=43.20$; $\rm H=2.15$. 0.1630 ,, 28.5 c.c. of moist nitrogen at 14° and 758 mm. $\rm N=20.5$. $\rm C_{10}H_4N_2O_4(N\cdot OH)_2$ requires $\rm C=43.17$; $\rm H=2.16$; $\rm N=20.1$ per cent.

Semicarbazons.—To the solution of the quinone in warm concentrated hydrochloric acid was added a warm solution of semicarbazine hydrochloride in moderately strong hydrochloric acid. After a few minutes, the greenish-yellow semicarbazone separated as a flocculent, crystalline precipitate. When cold, it was drained on the pump, washed with distilled water, and finally air dried.

0·1050 gave 0·1525 CO₂ and 0·0270 H₂O. C = 39·55; H = 2·85. 0·1077 ,, 28·47 c.c. moist nitrogen at 20° and 769 mm. N = 30·71 $C_{10}H_4N_2O_4(N_3H_3CO)_2$ requires C = 39·78; H = 2·76; N = 30·93 per cent.

Hexahydroxy-
$$\beta\beta$$
-dipyridyl, OH OH OH OH.

When the bronze-green derivative is treated with stannous chloride or tin and hydrochloric acid, it is converted into hexahydroxy- $\beta\beta$ -dipyridyl hydrochloride. This substance was boiled with benzoyl chloride and the filtered solution placed in a desiccator over caustic

potash. A white, crystalline, benzoyl derivative was formed, which was drained on the pump, washed with a little benzoyl chloride and dry benzene, and dried in a vacuum over solid paraffin; it melted sharply at 185°. On analysis,

0.1077 gave 0.033 H_2O and 0.2809 CO_2 . C = 71.12; H = 3.58. $C_{10}H_2N_2O_6(CO \cdot C_6H_5)_6$ requires C = 71.23; H = 3.65 per cent.

Dichlorodihydroxy-
$$\beta\beta$$
-dipyridylene oxide, OH N O N

To prepare this compound, the bronze-green derivative is just covered with chlorosulphonic acid, which must be added very slowly, as the reaction is very violent; the mixture is then heated at 100° on the water-bath for 15 minutes, and, after cooling, the dark-brown solution is poured into a litre of 50 per cent. acetic acid, left for 24 hours, and the heavy brown precipitate which forms is then filtered off on the pump and washed with a little acetic acid. It is next recrystallised from hot glacial acetic acid, and the process repeated two or three times, using a little animal charcoal. It is finally obtained as a white substance, which, under the microscope, is found to consist of a cluster of fine needles. It was dried in the air, and finally at 100°; the yield being 3.5 grams from 10 grams of the bronze-green derivative.

0.1250 gave 0.2040 CO_2 and 0.0184 H_2O . C=44.46; H=1.64.

0.1679 , 0.2731 CO_2 , 0.0238 H_2O . C = 44.38; H = 1.58.

0.1428 , 12.4 c.c. of moist nitrogen at 15° and 754 mm. N = 10.14.

0.1160 , 0.1236 AgCl. Cl = 26.35.

 $C_{10}H_4N_2Cl_2O_8$ requires $C=44\cdot28$; $H=1\cdot47$; $N=10\cdot33$; $Cl=26\cdot19$ per cent.

The substance dissolves readily in ether, alcohol, and acetone, but is insoluble in water. The ether employed in the molecular weight determination was prepared from absolute alcohol and dried carefully over sodium.

0.2217 in 21 c.c. of ether gave 0.11° elevation. Mol. wt. = 290. 0.3030 ,, 21.5 c.c. ,, ,, 0.16° ,, Mol. wt. = 273. $C_{10}H_4N_2Cl_3O_3$ has a mol. weight of 271.

Sodium Salt.—The chlorine derivative dissolves readily in sodium carbonate, from which the white sodium salt crystallises out on standing. This was drained on the pump, washed with a little water, and then dried in the air.

 $0.106 \text{ lost } 0.0153 \text{ at } 130^{\circ}$. $H_2O = 14.43$.

 $0.0907 \text{ dry salt gave } 0.0392 \text{ Na}_2\text{SO}_4. \text{ Na} = 11.98.$

 $C_{10}H_2Cl_2N_2O_3Na_2 + 3H_2O$ requires $H_2O = 14.60$; Na = 12.47 per cent.

Acetyl Derivative.—The substance was dissolved in boiling acetic anhydride and filtered; on cooling, the acetyl derivative crystallised out in white, micaceous scales which were washed with glacial acetic acid, and dried in the air. The nitrogen and chlorine were determined.

Benzoyl Derivative.—This was prepared by boiling the substance with benzoyl chloride, and, after filtering, placing in a desiccator over caustic potash. The benzoyl derivative crystallised out in clusters of white needles.

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0.1157 gave 0.2518 CO<sub>2</sub> and 0.0258 H<sub>2</sub>O. C = 60.09; H = 2.48. C_{10}H_2N_2Cl_2O_3(CO\cdot C_6H_5)_2 requires C = 60.12; H = 2.50 per cent.
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University Laboratory, Cambridge.

L.—The Condensation of Oxalic Acid and Resorcinol.

By John Theodore Hewitt and Arthur Ernest Pitt.

THE condensation of oxalic acid and resorcinol has been studied by various chemists, interaction being induced either at high temperatures or by the use of a condensing agent.

Apparently, the first to study the reaction was A. von Baeyer (Ber., 1871, 4, 662), who stated that, on heating with sulphuric acid, a yellow substance was obtained which does not exhibit fluorescence in solution, and is apparently similar to euxanthone, with the exception that it cannot be sublimed. Von Baeyer, nevertheless, thought it probable that the substance was a mixture in which euxanthone was present. The next work on the subject was that of Claus and Andreae (Ber., 1877, 10, 1305), who heated a mixture of resorcinol (1 mol.) with dehydrated oxalic acid (2 mols.) in sealed tubes for 2 to 3 hours at 200°; the product was mixed with alcohol and poured into water, a substance being thrown down which was purified by solution in alcohol and reprecipitation by water. When dissolved in alkalis, it shows a moss-green fluorescence, which is always exhibited, no matter how many times the substance has been taken up by alcohol. The

formula, $C_{18}H_8O_4$, assigned to this substance was afterwards altered in a later paper by Claus (*Ber.*, 1881, 14, 2563) to $C_{20}H_{14}O_7$ or $C_{20}H_{12}O_6$, the composition depending on whether it was dried at 100° or 150° . The results obtained by Claus on analysing the substance and its numerous derivatives led him to give to the first product of condensation and to its anhydride the formulæ I and II respectively.

Between the appearance of these two papers by Claus, Gukassianz (Ber., 1878, 11, 1184) studied the condensation of crystallised oxalic acid and resorcinol at 120° when heated for 4 or 5 hours with strong sulphuric acid, and observed in this way the formation of two substances, to both of which he assigned the empirical formula C₁₄H₈O₆. Moreover, he laid stress on the fact that the oxalic acid reacted as such, and not as carbon monoxide or dioxide, since the quantities of these two gases evolved were very small and practically in equivalent pro-Having first removed sulphuric acid and sulphonic acids by boiling with water, the product was dissolved in potassium hydroxide solution, precipitated by hydrochloric acid, and then taken up by alcohol. Most of the substance dissolved; a bright yellow residue was, however, left, which dissolved in alkalis, forming a yellowish-red solution showing a moss-green fluorescence. The alcoholic solution, on evaporation, left a dark brown mass which dissolved in potash easily, giving a brown solution destitute of fluorescence. The present communication is concerned with this latter substance.

During the progress of our work, a paper appeared by von Georgievics (Mitt. des. Technol. Gewerbe Museums in Wien, 1898, [ii], 8, 364; compare abstracts in J. Soc. Chem. Ind., 1898, 17, 837, and Chem. Centr., 1899, i, 284), in which the condensation of resorcinol with twice its weight of anhydrous oxalic acid by heating for 3 hours at 150—160°, without pressure or a condensing agent, is described. To the substance obtained, which was obviously different from those previously described, he gave the formula $C_{19}H_{12}O_6$, and its constitution was represented provisionally as

$$\mathrm{OH}\text{-}\mathrm{C}_{6}\mathrm{H}_{8}\!\!<\!\!\overline{\mathrm{O}\text{-}\mathrm{O}}\!\!>\!\!\mathrm{C}\!\!<\!\!\overline{\mathrm{C}}_{6}^{\mathrm{H}_{8}}\!\!(\mathrm{OH})\!\!>\!\!\mathrm{O}.$$

As the substance described by Gukassianz could not possibly have such a formula, we determined to proceed with its investigation.

Our attention was turned, in the first place, to the product which Gukassianz found to be soluble in alcohol, in the hope that it might prove to have some relationship with the hydroxyfluoronecarboxylic acid described by one of us and F. G. Pope (Ber., 1896, 29, 2824). The

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formula $C_{14}H_8O_5$ assigned by Gukassianz to the chief product of reaction is incorrect, and must be altered to $C_{20}H_{14}O_7$; this suggested that possibly the compound was identical with that obtained by Claus, the fluorescence of its alkaline solutions being explained by an incomplete separation from the substance sparingly soluble in alcohol. On investigating the matter further, we found that Claus' substance, although having the same molecular formula, was evidently different from that obtained by Gukassianz.

Acid C20 H14 O7.

The method we adopted for the preparation of this acid was essentially that described by Gukassianz, with several small modifications which conduced to the greater purity of the product. hundred and twenty grams of resorcinol (2 mols.), 126 grams of crystallised oxalic acid (1 mol.), and 126 grams of pure sulphuric acid of sp. gr. 1.84 were heated for 5 hours at 120°, and the product repeatedly extracted with boiling water, the filtrates depositing a bright yellow, flocculent substance on cooling. The residue, insoluble in water, was then boiled with methylated spirit, the bright yellow. sparingly soluble residue being added to the substance deposited from the aqueous extracts. The alcoholic solution was distilled on the water-bath, the residue boiled with an excess of sodium carbonate solution, filtered, and acidified with hydrochloric acid. The precipitate obtained, after being collected and washed with boiling water, was extracted with water in a Soxhlet's apparatus for 2 days and the residue dissolved in hot alcohol, and thrown out of solution by the addition of boiling water. An alcoholic solution of the acid deposits small crystals on slow evaporation; if, however, the extraction with water is not thoroughly carried out, the alcoholic solution leaves the substance as a varnish on evaporation.

The acid so obtained gives alkaline solutions, exhibiting not the slightest fluorescence; it dissolves in concentrated sulphuric acid with a dark brown coloration, whilst the crude acid containing traces of the fluorescent substance gives, under similar circumstances, a green solution. The acid is very soluble in aniline and ethylic alcohol, soluble in ether, acetone, glacial acetic acid, and amylic alcohol; sparingly soluble in chloroform, benzene or its homologues and in nitrobenzene, but insoluble in carbon bisulphide and light petroleum.

For analysis, the substance was dried, sometimes at 90—100°, and sometimes at 150—160° during 5 hours.

0.1283 dried at 100° gave 0.3048 CO_2 and 0.043 H_2O . C = 64.79; H = 3.72. 0.1159 dried at 160°, 0.2818 CO_2 , 0.040 H_2O . C = 66.31; H = 3.85. $C_{20}H_{14}O_7$ requires C = 65.57; H = 3.83 per cent.

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Gukassianz found, in the substance dried at $130-135^{\circ}$, $C=65\cdot62$, $65\cdot77$; $H=3\cdot5$, $3\cdot33$; nevertheless, it will be seen later that various compounds obtained from it are derivatives of a substance of the formula $C_{20}H_{12}O_6$, which stands to that just described in the relationship of lactone to acid.

Salts of the Acid.—On boiling an excess of the acid with dilute alkali carbonates until all evolution of carbon dioxide has ceased, salts of the type $C_{20}H_{18}O_7M'$ are produced, from which the conclusion may be drawn that two oxygen atoms are present as a carboxyl group.

The sodium salt, $C_{20}H_{18}O_7Na$, is very soluble in water or alcohol, and was thrown down from solution, after evaporating to a syrup, by the addition of acetone. The small red leaflets so obtained were dried at 110° until the weight was constant.

0.2800 gave 0.0480 Na₂SO₄. Na = 5.55. $C_{20}H_{13}O_7$ Na requires Na = 5.92 per cent.

The solution of the sodium salt gave the following precipitates with solutions of metallic salts.

Silver Nitrate: —In a concentrated solution, reddish-brown precipitate, rather soluble in pure water.

Calcium, Strontium, and Barium Chlorides: -- Red, crystalline precipitates, sparingly soluble in cold water.

Magnesium Chloride :- Light red precipitate.

Cadmium Sulphate: - Light reddish-brown precipitate.

· Manganese Chloride :- Red precipitate.

Cobalt Chlorids :- Red precipitate.

Copper Chloride: - Dark red precipitate.

Mercuric Chlorids:—Precipitate in concentrated solution, the salt is soluble in pure water.

Lead Nitrate: - Dark red precipitate, quite insoluble.

Aluminium Chloride: -Light red precipitate.

Ferric Chloride: -Blood red precipitate.

Of the above, the *lead* salt was prepared in larger quantity by dissolving the acid in dilute ammonia, expelling the excess of ammonia by boiling, and precipitating with lead acetate solution. The precipitate was collected, washed with boiling water to which a few drops of acetic acid had been added, and dried; it forms a dark mass with a strong green lustre recalling that of a beetle's wing.

0.2667 gave 0.0834 PbSO₄. Pb = 21.36. $(C_{20}H_{18}O_7)_2$ Pb requires Pb = 22.09 per cent.

Acetylation of the Acid C20 H14O7.

The acetylation of the acid was carried out by boiling with an excess of acetic anhydride; we found, however, that if the acetylated product was treated with aqueous alcohol, the compound which was isolated differed from that obtained when the use of liquids which could effect hydrolysis was avoided.

Triacetylated Lactons, C₂₀H₉O₆(CO·CH₃)₃.—Three grams of the pure acid were boiled for 2½ hours with 15 grams of acetic anhydride, and the product was poured into an amount of xylene sufficient to precipitate the acetylated compound in the cold; on heating, all went into solution, and on cooling, the acetyl derivative separated in small brown crystals. These were collected, washed with xylene and dried.

These figures show that water was eliminated and three acetyl groups introduced during the heating with acetic anhydride.

Triacetylated Acid, C₂₀H₁₁O₇(CO·CH₈)₈.—In our first experiment with regard to acetylation, we heated 2 grams of the acid with 2 grams of fused sodium acetate and 6 grams of acetic anhydride for 1 hour at 150°, poured the product into aqueous alcohol (50 per cent.), and washed first with 50 per cent. alcohol, and then with water. The small crystals obtained by recrystallisation from glacial acetic acid were collected, washed, and dried. It is very soluble in acetone and chloroform, soluble in glacial acetic acid, ethylic and amylic alcohols, aniline, and nitrobenzene, sparingly so in ether benzene, and toluene, and insoluble in carbon bisulphide, light petroleum, and xylene.

Analysis showed that this substance differed from that produced when water was excluded in the process of purification in containing the elements of an additional molecule of water.

0.1453 (dried at 108°) gave 0.3378
$$CO_2$$
 and 0.0540 H_2O . $C = 63.40$; $H = 4.13$. $C_{20}H_{11}O_7(C_2H_8O)_3$ requires $C = 63.41$; $H = 4.07$ per cent.

The easy transformation from the acetylated lactone to the acetylated acid on contact with aqueous alcohol recalls the behaviour of the benzoyl derivative of diorcylacetic acid (Hewitt and Dixon, Trans., 1898, 73, 397). The acetylation of the acid shows that the acid and its lactone must be represented by the formulæ $C_{19}H_9O(OH)_4COOH$ and $C_{19}H_9O(OH)_8 \stackrel{CO}{\longleftrightarrow}$ respectively.

To find out the character of the remaining oxygen atom, we resorted to acetylation in presence of zinc dust. If the oxygen were combined with two different carbon atoms, as in an ether, no change would be expected; if, on the other hand, the oxygen were united by a double linking to one carbon atom, as in a quinonoid compound, it should be reduced and acetylated under the conditions mentioned. The coloured nature of the substance certainly supported the latter view, and this was confirmed by the experimental results.

Acetylated Lactone, C₂₀H₁₀O₆(CO·CH₃)₄.—Five grams of the acid, 5 grams of zinc dust, 20 grams of acetic anhydride, and 10 grams of glacial acetic acid were boiled together for 3 hours; the colour having quite disappeared, the solution was poured into 50 per cent. aqueous alcohol, and the precipitate collected and dried on a porous tile. Purification was effected by dissolving it in chloroform, adding benzene, and slowly crystallising. The small crystals thus obtained were at first colourless, but on exposure to the air rapidly became red by oxidation. It is soluble in warm acetic acid, acetone, and chloroform, and only sparingly soluble or insoluble in hydrocarbon solvents or ether. It was analysed, with the following result:—

```
0.1791 gave 0.4264 CO_2 and 0.0626 H_2O. C = 64.93; H = 3.88. C_{20}H_{10}O_6(C_2H_8O)_4 requires C = 64.86; H = 4.25 per cent.
```

The functions of all the oxygen atoms in the molecule seem thus to be accounted for.

Benzoylation of the Acid $C_{20}H_{14}O$.

Benzoylation was effected by boiling the acid with five times its weight of benzoyl chloride for 1 hour. The readiest way of isolating the benzoyl derivative is to pour the product into an excess of light petroleum, filter, and wash with the same solvent; a pink, crystalline powder can be obtained by dissolving in chloroform and precipitating with either light petroleum or alcohol. The results given by different preparations of the substance, on analysis, did not, however, agree with those required for any possible benzoyl derivative of the acid or lactone, but accord best with those for the empirical formula $C_{21}H_{12}O_6$.

Such a formula might possibly represent a substance of the formula $C_{14}H_7O_6 \cdot CO \cdot C_6H_5$; 1 gram of the benzoate was therefore hydrolysed by boiling for 4 hours with 1 gram of sodium hydroxide and 10 grams of water. Hydrochloric acid was added to the solution while hot,

and the precipitated substance collected, well washed, dissolved in dilute ammonia solution, filtered, reprecipitated by hydrochloric acid, collected, washed, and dried. Its general appearance, slight solubility in most organic solvents, and the colour of its alkaline solutions showed the greatest resemblance to the hydroxyfluoronecarboxylic acid obtained by the breaking down of citraconfluorescein, and a benzoyl derivative of this acid might arise from such a reaction as the following:—

$$\label{eq:continuous} \begin{split} &C_{20}H_{14}O_7 + 3C_6H_5COCl = C_{14}H_7O_5(C_7H_5O) + C_6H_4(OC_7H_5O)_2 + 3HCl. \end{split}$$
 We give this equation, however, with reserve.

Nitration of the Acid C20H14O7.

When nitric acid of sp. gr. 1.42 is added to the finely divided acid suspended in an excess of glacial acetic acid, or when the substance is added in small quantities at a time to carefully cooled nitric acid and the operation carried out with care, two nitro-groups are introduced into the molecule.

On the other hand, if the reaction is allowed to proceed energetically, the nitric acid seems to act also as an oxidising agent, for the product obtained in this way is sensibly soluble in water, and on analysis shows a higher percentage of nitrogen and a lower one of carbon. This effect does not seem to be due to the further introduction of nitro-groups, since it was observed that gas was evolved during the process, and that the weight of nitrated acid obtained was considerably less than the weight of non-nitrated acid used for the experiment, whilst with a carefully conducted experiment, the weight of nitro-acid obtained should be greater than that of the substance employed.

We consequently adopted the following process:—50 grams of nitric acid of sp. gr. 1.42 were well cooled by running water, and 10 grams of the finely divided substance added in small quantities at a time; after it had all been added, the mixture was left for 5 hours, then poured into water, and the precipitated nitrated compound collected and well washed with warm water. After drying, first on a porous tile and then at 70°, the weight of the product was found to be 11 grams.

The nitro-compound is very soluble in acetone, and dissolves fairly easily in alcohol and acetic acid; advantage may be taken of this solubility for effecting its purification, the substance being thrown out as a bright brown, crystalline powder on adding acetic acid to its solution in acetone. It may be added that it is very sparingly soluble in ether and amylic alcohol, and quite insoluble in chloroform, carbon

bisulphide, and hydrocarbon solvents. Analysis showed that it has the formula $C_{20}H_{10}O_6(NO_2)_2$, and not $C_{20}H_{12}O_7(NO_2)_2$, as had been expected.

```
0.1672 gave 0.3358 CO<sub>2</sub> and 0.0499 H<sub>2</sub>O. C=54.41; H=3.31. 0.2061 ,, 0.4089 CO<sub>2</sub> ,, 0.0426 H<sub>2</sub>O. C=54.11; H=2.29. 0.1937 ,, 10.65 c.c. nitrogen at 14° and 754.5 mm. N=6.4. 0.1854 ,, 9.6 ,, , 16° ,, 776.0 mm. N=6.1. C_{20}H_{10}O_{6}(NO_{2})_{2} requires C=54.79; H=2.29; N=6.39 per cent.
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The high results for carbon, supposing the compound was $C_{20}H_{12}O_7(NO_2)_2$, caused us to think that perhaps it contained a small admixture of the non-nitrated acid; we therefore, before making the second carbon estimation, converted it successively into the ammonium and barium salts, washed the latter thoroughly with boiling water, in which the barium salt of the non-nitrated acid is appreciably soluble, decomposed the barium salt with hydrochloric acid, dissolved in ammonia, reprecipitated with hydrochloric acid, washed thoroughly, and dried. On account of the explosive nature of the nitro-compound, the analyses were carried out in a bayonet tube, with a reduced copper spiral.

Salts of Nitrated Acid.—The sodium salt of the nitrated acid was prepared by boiling the substance with a solution of one-eighth of its weight of pure sodium carbonate until all evolution of carbon dioxide had ceased; the solution was then filtered from the excess of acid, and evaporated to dryness. The saline residue, after extraction with alcohol, was dried at 100°.

```
0.5297 sodium salt gave 0.078 Na<sub>2</sub>SO<sub>4</sub>. Na = 4.77. C_{20}H_{11}O_7(NO_2)_2Na requires Na = 4.62 per cent.
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The aqueous solution of the sodium salt gave dark red precipitates with strontium, barium, magnesium, manganese, cobalt, copper, aluminium, or ferric chlorides, and with cadmium sulphate; the silver and mercuric salts, however, are soluble.

Acetylation.—The nitrated substance was boiled for 1½ hours with five times its weight of acetic anhydride, xylene being then added to produce a separation of solid matter; on boiling, the precipitate was dissolved, and came down again on cooling as small, light red crystals. These were collected, washed with xylene, and dried first at 70° and then over sulphuric acid.

The acetyl derivative is very soluble in acetone, aniline, and nitrobenzene, soluble in acetic acid, and ethylic alcohol, sparingly so in chloroform, and insoluble in carbon bisulphide, ether, amylic alcohol, and hydrocarbon solvents. Analysis showed the substance to be a triacetylated dinitro-lactone.

Bromination.—On bromination, the acid formed a tetrabrominated product. Ten grams of the acid were suspended in 50 c.c. of glacial acetic acid, and 20 grams of bromine were gradually added, the liquid being kept cool during the process. When all the bromine had been added, the mixture was left for 1 hour and then poured into water. The precipitate was collected, washed, dissolved in sodium hydroxide solution, and reprecipitated by hydrochloric acid. The brominated acid is very soluble in acetone and ethylic alcohol, soluble in acetic acid and aniline, sparingly so in ether and nitrobenzene, and insoluble in amylic alcohol, carbon bisulphide, chloroform, and hydrocarbon solvents.

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0.2000 gave 0.2564 CO<sub>2</sub> and 0.0273 H<sub>2</sub>O. C=34.97; H=1.52. 0.3274 ,, 0.3693 AgBr. Br=47.99. C_{20}H_{10}Br_4O_7 requires C=35.19; H=1.46; Br=46.92 per cent.
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The brominated acid dyes silk of a colour resembling that imparted by eosine, but it is not so brilliant. A solution of the sodium salt of this acid gives purplish-red precipitates with salts of the heavy metals, the silver salt in this case being insoluble; the mercuric salt is, however, soluble in pure water. The barium salt contained 8.9 per cent. of Ba (calculated = 9.1 per cent.).

Our work shows that the chief product of the interaction of oxalic acid and resorcinol, when heated with concentrated sulphuric acid at 120° , is a substance of the formula $C_{20}H_{14}O_7$, which is isomeric, and not identical, with the compound described by Claus, as the latter, unlike our acid, loses a molecular proportion of water at 150° . Moreover, Claus' compound forms tetranitro- and pentabromo-derivatives, whereas our substance takes up only two nitro-groups or four bromine atoms; further, the non-fluorescent compound we have studied is not apparently in any way derived from the fluorescent substance produced at the same time, as, after heating together a mixture of the yellow substance which gives fluorescent alkaline solutions ($C_{14}H_8O_5$, or perhaps also $C_{20}H_{14}O_7$) with resorcinol and sulphuric acid for some time, we could not detect the non-fluorescent substance in the product.

The substance having the formula $C_{19}H_{12}O_6$, described by von Georgievics, is evidently not a condensation product of resorcinol

with oxalic acid as such, so that the compound described by Gukassianz does not appear to have been examined by other investigators. Gukassianz, however, misinterpreted the results of his analyses, a very easy matter, as is seen when the percentage compositions required by the formulæ C14H2O4 and C20H14O2 res-The presence of one carboxyl group is inpectively are compared. dicated by the analyses of the sodium and lead salts, and also that of the sodium salt of the nitrated acid. Acetylation shows that three hydroxyl groups remain after the lactone has been formed at the expense of the carboxyl radicle and one of the hydroxyl groups; the remaining oxygen atom is of a quinonoid character, as is shown by the composition of the acetylated lactone, obtained in the presence of zinc dust. The formula of the acid may, therefore, be written thus, O:C₁₀H₀(OH)₄(COOH), or as the substance is evidently formed by condensation of 1 mol. of oxalic acid with 3 mols. of resorcinol, its formula may be written as [O:C₁₈H₀(OH)₄]:C·COOH. Until some well-defined hydrocarbon can be obtained by the reduction of the compound, further views as to its constitution can only be of a speculative character.

EAST LONDON TECHNICAL COLLEGE.

LI.—Synthesis and Preparation of Terebic and Terpenylic Acids.

By W. TREVOR LAWRENCE.

TEREBIC acid, $C_7H_{10}O_4$, and terpenylic acid, $C_8H_{12}O_4$, are the chief products of the oxidation of oil of turpentine, and their investigation has thrown much light on the difficult question of the constitution of the terpenes. The yield of the first of these acids by this process is unsatisfactory, and the author has succeeded in finding a more convenient method for its preparation; he has also succeeded in preparing terpenylic acid synthetically. A short account of these experiments forms the subject of this paper.

Terebic Acid.

The constitution of terebic acid has been established for some years (Fittig and his pupils, *Annalen*, 1881, 208, 37, 55; 1883, 220, 254; 1884, 226, 363), and is that of the lactone of γ -hydroxyisopropyl

succinic acid, the formula being (CH₈)₂C——CH·COOH
O·CO·CH_a
The acid

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has been prepared synthetically in various ways, of which, however, only two are of practical importance.

Blaise (Compt. rend., 1898, 126, 349) obtained a yield of 10 to 12 per cent. of the theoretical amount of terebic acid by the condensation of ethylic bromosuccinate with acetone in the presence of a zinc copper couple:

$$\begin{array}{ll} {\rm COOEt \cdot CH_2 \cdot CHBr \cdot COOEt} + {\rm CH_3 \cdot CO \cdot CH_3} + {\rm Zn} \\ & = ({\rm CH_3)_2 C (OZnBr) \cdot CH} < \begin{array}{c} {\rm CH_2 \cdot COOEt} \\ {\rm COOEt} \end{array}, \end{array}$$

the ethylic salt passing, on hydrolysis, into terebic acid.

Fittig converted dimethylitaconic acid (Annalen, 1884, 226, 365) (teraconic acid) and dimethylaticonic acid (Annalen, 1899, 304, 220) quantitatively into terebic acid by heating with 50 per cent. sulphuric acid.

As I required large quantities of terebic acid in order to perform experiments, in conjunction with Dr. A. W. Crossley, on the action of hydrobromic acid on this substance, it was necessary to devise a simpler and more economical method of preparation. Certain considerations, which will be mentioned in discussing terpenylic acid, led me to oxidise isopropylsuccinic acid, in the hope that the reaction would proceed according to the equation:—

Isopropylsuccinic acid can be obtained by various synthetical methods, and forms 20 per cent. of the products of the fusion of camphor or camphoric acid with potash; it is easily oxidised by a mixture of potassium dichromate and sulphuric acid to terebic acid, which crystallises out in a pure condition from the oxidation mixture on cooling. The yield represents 50 to 60 per cent. of that theoretically possible, and a considerable amount of unchanged isopropylsuccinic acid is recovered, so that this method is more economical than any described up to this time.

Terpenylic Acid.

The investigations of Fittig (Annalen, 1884, 226, 374; 1895, 288, 185), Schryver, and Mahla and Tiemann showed that the constitution of terpenylic acid agrees with the formula suggested by Wallach (Annalen, 1890, 259, 321),

$$(CH_8)_2C$$
—— $CH \cdot CH_2 \cdot COOH$.

The proof is, briefly, as follows. When terpenylic acid, $C_8H_{12}O_4$, is distilled, teracrylic acid, $C_7H_{12}O_2$, is formed, and this is converted by the action of hydrobromic acid into the isomeric heptolactone.

Schryver (Trans., 1893, 63, 1332) synthesised this heptolactone and proved that it had the formula

$$(CH_s)_2$$
C — $CH \cdot CH_s$
 $O \cdot CO \cdot CH_s$

Moreover, the same investigator obtained β -isopropylglutaric acid by reducing terpenylic acid with sodium amalgam:

and prepared this glutaric acid by the condensation of ethylic isobutylenemalonate with ethylic malonate:

$$\begin{aligned} (\mathrm{CH_3})_2\mathrm{CH}\text{-}\mathrm{CH}\text{:}\mathrm{C(COOEt)}_2 &+ \mathrm{CH_2}(\mathrm{COOEt)}_2 \\ &= (\mathrm{CH_3})_2\mathrm{CH}\text{-}\mathrm{CH} \underbrace{\overset{\mathrm{CH}(\mathrm{COOEt})_2}{\mathrm{CH}(\mathrm{COOEt})_2}}. \end{aligned}$$

Finally, Mahla and Tiemann (Ber., 1896, 29, 928), in a paper reviewing the question of the constitution of terpenylic acid, confirmed Wallach's formula by converting this acid into terebic acid by oxidation with potassium permanganate.

$$(CH_2)_2C ---CH \cdot CH_2 \cdot COOH + 3O$$

$$= (CH_3)_2C ----CH \cdot COOH + CO_2 + H_2O.$$

The synthesis of this important acid still remained to be effected and is described in the present paper.

The classical researches of R. Meyer (Annalon, 1893, 219, 214, 220, &c.), and of Fittig and Bredt (Annalon, 208, 1881, 59, &c.), have shown that acids having a tertiary hydrogen atom are capable of direct oxidation to hydroxy-acids by means of potassium permanganate in alkaline solution.

By kind permission of Dr. J. F. Thorpe, I was able to prepare

 β -isopropylglutaric acid in considerable quantities (Howles and Thorpe, Proc., 1899, 15, 103), and first attempted its oxidation by the method indicated by R. Meyer, but the acid remained apparently unchanged (compare, however, H. Thron, *Annalen*, 1899, 304, 285), even when dissolved in strong alkali and boiled with excess of 5 per cent. permanganate solution. It was consequently necessary to try other oxidising agents, and it was found that a mixture of potassium dichromate and sulphuric acid oxidised β -isopropylglutaric acid in 24 hours at the temperature of the water-bath, giving a 50 per cent. yield of terpenylic acid, agreeing in every particular with the acid obtained by the oxidation of oil of turpentine.

The synthesis of terpenylic acid has thus been accomplished, and I am at present preparing large quantities of the acid for the purpose of studying, with Professor W. H. Perkin, its behaviour with hydrobromic acid. I also wish to reserve the investigation of the oxidation of α-isopropylglutaric, α-methyl-α-isobutylglutaric and methylisoamyl-succinic acids.

EXPERIMENTAL.

Oxidation of Oil of Turpentine.

The oxidation of oil of turpentine was carried out by Fittig's method, but the products were purified in the following manner. As soon as the oil of turpentine (180 grams) had disappeared from the surface of the chromic acid liquors, these were saturated with ammonium sulphate, extracted several times with ether, and the ether extract distilled with steam to remove acetic and other fatty acids formed; the solution containing the non-volatile acids was then evaporated to a small bulk and left in a vacuum for two days over sulphuric acid. The nearly solid, crystalline mass thus isolated was dried by spreading it on porous plates, and ultimately obtained colourless and dry by transferring it to fresh plates and spreading uniformly by means of a little water.

By extracting these plates, 10 grams of a liquid acid or mixture of acids was obtained, but has not as yet been investigated.

The dry powder consisted of a mixture of terebic and terpenylic acids, and difficulty was anticipated in their separation (compare Mahla and Tiemann, Ber., 1896, 29, 933). It was found, however, that if the finely ground powder was spread on porous plates and heated in the steam oven at 90°, a complete separation was effected in one operation, the terebic acid remaining as a crystalline powder on the surface of the plate and the terpenylic acid being completely absorbed. The terpenylic acid was recovered with practically no loss

^{*} Extremely absorbent plates were obtained from Messrs: Doulton, of Lambeth.

by extracting the plates with water, and both acids were recrystallised from this solvent. The yield of pure terebic acid represents 5 per cent. and that of terpenylic acid 15 per cent. of the weight of the oil of turpentine oxidised. The terpenylic acid thus obtained melts at 56° to a clear liquid, whereas two specimens of the acid sold as pure contained a considerable amount of terebic acid. My thanks are due to Mr. H. Marsden, a student of the Owens College, for the careful way in which he has conducted this part of the investigation.

Synthesis of Terebic Acid.

A solution of 10 grams of isopropylsuccinic acid (pimelic acid), in 150 c.c. of water, was added to a mixture of 40 grams of potassium dichromate with 55 grams of sulphuric acid, and heated on the waterbath for 56 hours; the mixture, after being left for 2 days, became filled with a white, crystalline substance mixed with crystals of dichromate. The crystals were collected, washed with water, dried on a porous plate, and the finely powdered mixture of terebic acid and potassium dichromate boiled with ether and filtered from the inorganic salt. On evaporating the ether, 5.5 grams of terebic acid were obtained, which, after being purified by recrystallisation from water, melted at 175°, and on analysis gave the following numbers:

0.1241 gave 0.2412 CO₂ and 0.0740 H₂O. C=53.07; H=6.6. $C_7H_{10}O_4$ requires C=53.16; H=6.33 per cent.

The identity of the acid was confirmed by mixing some of the synthetical acid with the acid obtained by the oxidation of oil of turpentine; this mixture melted sharply at 174°.

The characteristic barium salt of the hydroxy-acid was also prepared by boiling the solution of terebic acid with excess of baryta, removing the excess of base with carbon dioxide, and precipitating the barium terebinate with alcohol.

 $0.2113 \text{ gave } 0.1337 \text{ BaSO}_4$. Ba = 37.2. $C_7H_{10}O_5Ba + 3H_2O$ requires Ba = 37.53 per cent.

After the crystals of terebic acid had been filtered off, the chromic acid liquors were saturated with ammonium sulphate, and on extraction with ether, an oil smelling strongly of acetic acid was obtained, which, when left, deposited 2.5 grams of isopropylsuccinic acid.

Synthesis of Terpenylic Acid.

Before the correct oxidising agent was found in chromic acid mixture, an attempt was made to oxidise β -isopropylglutaric acid by means of potassium permanganate and of nitric acid; with fuming

nitric acid, a liquid acid was obtained, the constitution of which was not determined. A concentrated solution of the acid in strong caustic potash was next treated with excess of a saturated solution of potassium permanganate at the temperature of the water-bath; the acid was, however, recovered unchanged, and no oxidation product could be isolated.

The oxidation of β -isopropylglutaric acid, which led to the formation of terpenylic acid, was carried out as follows: 2.5 grams of pure β -isopropylglutaric acid (m. p. 101°) were dissolved in 15 c.c. of water and added to a mixture of 5 grams of potassium dichromate with 6 grams of sulphuric acid, and heated on the water-bath for 48 hours. At the end of this time, the dark green liquors were saturated with ammonium sulphate and extracted with ether several times; the ethereal solution, on evaporation, yielded a crystalline substance which was recrystallised from water, and gave 1.3 grams of pure terpenylic acid. From the mother liquors, 1 gram of β -isopropylglutaric acid was recovered. The acid was dried over sulphuric acid in a vacuum to remove the water of crystallisation, and on analysis gave the following figures:

Synthetical terpenylic acid agrees in every particular with the oxidation product from oil of turpentine. It crystallises from water with $1\rm{H}_2\rm{O}$, and melts at 56° ; the water of crystallisation is removed by exposure over sulphuric acid, and the melting point then rises to 89°; moreover, a mixture of the synthetical acid with the acid obtained by the oxidation of oil of turpentine melts at the same temperature as each of its constituents.

The characteristic silver salt is obtained either by adding excess of silver carbonate to the concentrated solution of the acid and filtering off the excess, or by adding a solution of silver nitrate to the ammonium salt; in both cases, the liquid remains clear for a few minutes, and then becomes filled with the beautiful needles of the silver salt, which is very soluble in hot water.

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0.0380 gave 0.0148 Ag. Ag = 39.00.

C_sH_{11}O_4Ag requires Ag = 39.00 per cent.
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To further establish the identity of the synthetical acid, it was oxidised by a 5 per cent. solution of potassium permanganate, according to the method described by Mahla and Tiemann (*loc. cit.*). The mixture of terpenylic and terebic acids extracted from the product of this experiment was recrystallised from water, and the two acids separated by the method indicated earlier in this paper, when it was found

that a considerable proportion of the terpenylic acid had been oxidised to terebic acid melting at 175°.

A proof that the tertiary hydrogen atom in isopropylsuccinic and β -isopropylglutaric acids undergoes oxidation was afforded by attempting to oxidise 5 grams of $\beta\beta$ -dimethylglutaric acid in a similar manner with chromic acid mixture; after 60 hours treatment, the liquors were extracted, and 4.8 grams of unchanged $\beta\beta$ -dimethylglutaric acid, melting at 101° , were obtained. A negative result was also obtained with β -monomethylglutaric acid.

THE OWENS COLLEGE.

LII.—Ethyl Ammoniumsulphite.

By Edward Divers and Masataka Ogawa.

In attempts to obtain ammonium amidosulphite, which proved successful only when made in another direction, we found that, in absence of water and at a low temperature, ammonia and alcohol unite with sulphur dioxide to form a new salt, which, although it has the same composition as ammonium ethylsulphonate, is quite distinct from it. Evidently, ammonia and alcohol react with sulphur dioxide as though they were ethylammonium hydroxide, for ammonia in the cold has no action either on ethyl sulphite or on ethyl ethylsulphonate, and when heated with the former produces ethylamine and ammonium sulphite (Carius, Annalon, 1859, 110, 221), and with the latter, ethylammonium ethylsulphonate (Carius, J. pr. Chom., 1870, [ii], 2, 262).

Warlitz's so-called potassium ethyl sulphite has since been shown to be potassium ethylsulphonate (Rosenheim and Liebknecht, Ber., 1898, 31, 405), and from the experiments of Carius, and from those of the chemists just named, it is also certain that ethyl sulphite does not react directly to form a salt intermediate between itself and potassium sulphite, and is thus distinguished from a sulphonate, as Carius pointed out (see also the action of ammonia, just referred to above).

Within the last few years, however, a new class of alkyl metallosulphites has come to be known, and in this class the new ethyl ammonium-sulphite must be placed. The first member discovered was phenyl sodiumsulphite (Schall, Ber., 1892, 25, 1875; J. pr. Chem., 1893, [ii], 48, 241), formed from sodium phenoxide and sulphur dioxide; next came methyl magnesiumsulphite, obtained by Szarvasy (Ber., 1897, 30, 1836), from magnesium methoxide and sulphur dioxide, and, lastly, methyl and ethyl sodiumsulphite and ethyl potassiumsulphite, prepared from sodium or potassium ethoxide or methoxide respectively, and sulphur dioxide (Rosenheim and Liebknecht, 1898, loc. cit.).

Schall has established that his salt is Na·SO₂·OC₆H₅, and Rosenheim and Liebknecht have given good reasons for regarding their salts, and also Szarvasy's salt, as similarly constituted—Na·SO₂·OC₂H₅; Mg(SO₂·OCH₃)₂, that is, as having a constitution complementary to that of sulphonates. Szarvasy, indeed, considers that his sulphite has a constitution analogous to that of the ethyl magnesium carbonate, which he obtained in a similar way, but, in doing so, he ignores what seems so well established, that sulphites behave as the analogues of formic acid and other carboxylic salts, rather than of carbonates, although producible in the same way as the latter salts.

Special precautions have to be taken to ensure the absence of water. Muspratt, on passing "dried" sulphur dioxide and ammonia into ether, was surprised to get ammonium pyrosulphite; Carius found that "carefully dried" sulphur dioxide formed only sodium sulphite when led into sodium ethoxide dissolved in "absolute" alcohol (the italics are his), although, as a fact, it does combine with the ethoxide. Both chemists had failed in their attempts to exclude water, and we, too, have failed to keep back all moisture. In 100 c.c. of concentrated alcoholic ammonia, we had never much less than 80 milligrams of water, but, fortunately, we were able to eliminate this, as anhydrous ammonium sulphite, which is insoluble in alcohol.

The absolute alcohol was distilled from lime directly into a flask, which was then closed by a dried cork provided with inlet and outlet tubes, the latter dipping into mercury as a seal; the ammonia, dried by recently fused potassium hydroxide, was passed into the alcohol in the flask, which was kept cool in a freezing mixture. When ammonia began to freely escape through the mercury seal, the current of gas was stopped, and sulphur dioxide, well dried by sulphuric acid, was passed in slowly until this also began to bubble freely through the mercury, the temperature being kept as nearly as practicable down to -15° and the flask frequently agitated. There are two reasons for keeping the temperature low; in the first place, the solution of ammonia in alcohol must be very concentrated, so as to convert the greater part of the alcohol into the new salt, as the latter is very soluble; moreover, the lew temperature prevents any of the sulphur dioxide from acting on the ammonia as an oxidising agent, thereby producing an orange coloured impurity (apparently nitrogen sulphide) and ammonium sulphite.

After passing in the sulphur dioxide for a short time, the turbid solution was allowed to clear and then decanted from a small deposit (0.5 gram or less) of anhydrous ammonium sulphite into another flask with as little exposure to air as possible; this sulphite represented the small amount of moisture present. The introduction of sulphur dioxide being resumed, transparent, four-sided prisms began to form

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when the ammonia was nearly saturated, and then increased so rapidly that nearly all the solution disappeared by the time the ammonia was all gone. If the operation was arrested at this point, the substance could not be obtained pure enough for analysis, partly on account of its exceedingly hygroscopic nature, and partly because the mother liquor contained a viscid, non-volatile substance, probably pyrosulphite, EtNaS₂O₅. The current of sulphur dioxide, therefore, was continued, as stated above, until much sulphur dioxide passed through unabsorbed. The crystals slowly dissolved, but whether this was due to their being dissolved in the sulphur dioxide, liquefied at the low temperature, or to the formation of pyrosulphite, is uncertain.

In order to obtain the salt in the solid state, the solution was poured, in portions suitable for analysis, into small flasks of ether freshly distilled from sodium. The two liquids, which did not mix, on gentle rotation, deposited the substance on the walls of the flask in a crystalline state, while much sulphur dioxide escaped. The ether was poured off, the crystals washed with more ether, dried rapidly in the desiceator, and weighed in the flask; the ether left no residue on evaporation.

The analysis of the salt was simple. Distillation with alkali gave the ammonia and alcohol, which were received in volumetric acid, the ammonia titrated, and the alcohol determined in the distillate after rectification. In order to be certain that no amidosulphonate had been formed, the alkali sulphite left in the distilling flask was heated in a pressure tube with hydrochloric acid, again rendered alkaline, and distilled. The sulphur dioxide was determined as barium sulphite in a separate portion of the salt after oxidising, first with bromine and alkali, and then with potassium chlorate and hydrochloric acid. The quantities of the salt serving for the analysis were about 2 grams in each case. The percentages were

 $C_2H_5(NH_4)SO_8$, alcohol; 36·22; ammonia, 13·38; sulph. diox., 50·39. Found, ,, 35·87; ,, 13·35; ,, 49·99.

Ethyl ammoniumsulphite is crystalline, and sublimes unchanged when heated in a dry tube. It is decomposed violently by strong sulphuric acid, but without blackening. Acids at once set free sulphur dioxide. It is insoluble in ether, but dissolves in alcohol without change, and can be recovered by evaporation, provided no trace of water is present. It is also in part precipitated from its concentrated solution in alcohol on saturating it with ammonia at a low temperature. It is exceedingly deliquescent, and is immediately decomposed by water, in which it dissolves. Its alcoholic solution at once crusts over when exposed to the air, ammonium pyrosulphite

being produced. The aqueous solution or deliquesced salt smells strongly of sulphur dioxide, and gives the reactions of a sulphite only in its fresh state, but from the tendency of pyrosulphite to change into trithionate, it becomes yellowish after a time, and its silver salt slowly changes colour. In a freshly-prepared solution, hydrochloric acid gives no precipitate of sulphur, and the acid solution loses all its sulphur as sulphur dioxide when quickly boiled.

Szarvasy found it necessary, in preparing methyl magnesiumsulphite, to saturate the alcoholic solution with sulphur dioxide, and for the reason above given we also found it advantageous to saturate the alcohol with sulphur dioxide in preparing the ethyl ammoniumsulphite. Rosenheim and Liebknecht, on the other hand, state that the use of any excess of sulphur dioxide in making the alkyl alkalisulphites is most carefully to be avoided, as otherwise these salts decompose into "acid" alkali sulphites. This difference between closely allied salts would be remarkable, and not easy to understand if its existence could be confirmed. In absence of water, pyrosulphites, rather than acid sulphites, alone can form, but if the unknown ethyl sodiumpyrosulphite had been the salt formed, these chemists would presumably not have failed to indicate the fact. Again, if sodium pyrosulphite and ethyl pyrosulphite had been the products, then the latter would also have been noticeable as a compound new to science. Szarvasy's and our own experience, and the difficulty of interpreting Rosenheim and Liebknecht's results, have caused us to prepare ethyl sodiumsulphite and test its behaviour with sulphur dioxide.

Sodium, bright and clean cut under dried ether, was quickly transferred to a little dry alcohol in a small flask until the solution thickened and no longer acted on fresh pieces of sodium, and the solution, quickly decanted in a cold, dry atmosphere into another flask, was cooled in a freezing mixture, which caused abundant crystallisation of sodium ethoxide. Sulphur dioxide was now passed in until it was in large excess in the liquefied state; its effect was to cause the sodium ethoxide to dissolve gradually and give place to the micaceous crystals of Rosenheim and Liebknecht's salt, until the solution had almost all dried up. After this, it appeared to have no further action. The very sulphurous mother liquor was drained off, the flask placed in a vacuum desiccator to dry its contents, the dry salt weighed in the preparation flask, and an aqueous solution of potassium hydroxide poured on to it. Oxidised, first by bromine and then by potassium chlorate and hydrochloric acid, it gave 24.67 per cent. of sulphur, thus confirming the observation that the salt did not seem to be. affected by excess of sulphur dioxide, for the calculated quantity of sulphur in ethyl sodiumsulphite is 24.24 per cent. We conclude, therefore, that Rosenheim and Liebknecht failed to guard sufficiently

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against the entrance of moisture, and that their salts are not destroyed by dry sulphur dioxide. The sulphur dioxide mother liquor poured off in our experiment was left for some time in an open flask, and was only then placed in a desiccator; it left a small quantity of sodium pyrosulphite as a white powder. The salt is therefore a little soluble in alcoholic sulphur dioxide, and then, by absorbing water, becomes changed into alcohol and sodium pyrosulphite.

LIII.—Ethyl Ammonium Selenite and the Non-existence of Amidoselenites (Selenosamates).

By Edward Divers and Seihachi Hada.

Ethyl Ammonium Selenite.

In absence of water, selenion dioxide proves to be quite indifferent to ammonia in the cold or to its solution in ether. Although not very soluble in alcohol alone, it dissolves freely in alcoholic ammonia to become, in absence of water, a new salt, ethyl ammonium selenite, obtainable in the solid state, either by evaporating the alcohol or by precipitating the salt with dry ether. Hinsberg (Annalen, 1890, 260, 40) has found that an alcoholic solution of selenion dioxide, free from all water, on evaporation, leaves crystals of ethyl hydrogen selenite, which slowly decompose again in dry air into alcohol and selenion dioxide, or at once, in contact with water, into alcohol and selenious acid. He also obtained what appeared to be the aniline salt of this compound, in an impure state, by mixing and evaporating solutions of selenion dioxide in alcohol and of aniline in ether, but only in absence of water. Water at once decomposed the salt into alcohol and the acid selenite of aniline.

The production of ethyl ammonium selenite acquires interest from the fact that it can only be effected in the entire absence of water, to the action of which the salt is very sensitive. The salt is also of interest because, in mode of formation and in properties, it closely resembles ethyl ammoniumsulphite (see preceding paper), although the work of Michaelis and Landmann (Annalen, 1887, 241, 150) seems to have established that nothing analogous to a sulphonic constitution presents itself in alkyl selenites. One of us has also pointed out (Trans., 1886, 49, 585) some special points of similarity of silver and mercury selenites to silver and mercury sulphites, although their alkyl derivatives are differently constituted (Michaelis and Landmann, loc. cit.).

The selenion dioxide for making the new salt was prepared from

selenion of high purity, which had been obtained, years ago, from the 'red sulphur' of Japan, by M. Shimosé and one of us; as the anhydride is very hygroscopic, special care had to be taken to ensure its freedom from water when used; the selenion was dissolved in nitric acid, the solution evaporated to dryness, and the residue repeatedly moistened with water and dried again by heat. The selenious acid was then heated for some time, in an open dish, close to the subliming point of the anhydride. Thus almost dehydrated, it was transferred hot to a glass tube in which it was several times sublimed in a current of dry oxygen. Finally, it was again volatilised into and deposited in the well dried experimental vessel itself. Great care was also taken to dry the alcohol in the usual way, and then to keep it almost out of contact with the air. The ammonia, too, was well dried, not so effectively, perhaps, as the alcohol and the anhydride, yet sufficiently so as the result proved.

The selenion dioxide, with about five times its weight of alcohol, was treated with ammonia, in a freezing mixture, until the gas passed unabsorbed; the ammonia causes the undissolved selenion dioxide to dissolve slowly, and the final product is a clear, viscid liquid. This liquid, which is most sensitive to the decomposing action of the moisture of the air, can be dried up in a vacuum into a solid with silky lustre, but cannot be obtained in this way quite free from alcohol. Instead, therefore, of evaporating the liquid, it was poured into a small flask of well-dried ether with as little exposure to air as practicable; the liquid, as in the case of sulphite, does not dissolve in ether, but, on shaking, the ether extracts the alcohol from it and leaves the solid salt adhering to the flask. After decanting off the ethereal solution and exposing the open flask for a night in a vacuum desiccator, the salt was obtained dry and was then weighed in the flask.

In analysing the salt, it was dissolved in water acidified with sulphuric acid, the slightly acid liquid distilled, and the alcohol in the distillate determined in the usual way. Distillation of the solution with alkali gave the ammonia; the residue on being heated at 150° for some hours with hydrochloric acid, and again distilled with alkali, gave no more ammonia. The selenion was determined by precipitating it with sulphur dioxide in presence of much hydrochloric acid, heating to 100°, and collecting the selenion on a weighed filter. The mother liquor, after concentration, gave no more selenion with sulphur dioxide.

The percentage numbers obtained were

 $C_2H_5(NH_4)SeO_3$, sel. diox., 63·79; ammonia, 9·77; alc., 26·44 per cent. Found, , 64·09; , 9·31 , — ,, 65·94; , 10·09 , 24·16 ,,

The deviations of the quantities found from those calculated are clearly attributable to slight decomposition of the salt by moisture into alcohol lost, and acid ammonium selenite.

Ethyl ammonium selenite is crystalline, soluble in alcohol, insoluble in ether, exceedingly deliquescent, and at once decomposed by water into ammonium hydrogen selenite and alcohol. It cannot be heated or even kept long without decomposing, selenion being one of the products. Thus, after 10 days or so in the desiccator, the decomposed salt may contain as much as 5 per cent. of its weight of free selenion, oxidised alcohol (acetic acid t) and ammonia having volatilised.

Non-existence of Amideselenites (Selenosamates).

Since it is not easy to prepare normal ammonium selenite from its aqueous solution, on account of its great solubility and the readiness with which it loses much of its ammonia, Berzelius, Muspratt, and others have had resort to an alcoholic solution of selenious acid from which to precipitate the salt by gaseous ammonia. Now, when an alcoholic solution of ethyl ammonium selenite is exposed to moist air or mixed with a very little water, ammonium selenite separates at once, either normal or acid, according as much ammonia is present or The same behaviour has been noted by Hinsberg in an alcoholic solution of ethyl phenylammonium selenite; moreover, the behaviour of an alcoholic solution of ethyl ammonium sulphite is strictly analogous (see preceding paper). Accordingly, we have found that, unless precautions are taken to specially dry the materials and to exclude moisture, the passage of ammonia into a solution of selenion dioxide in good ordinary 'absolute' alcohol very soon causes the precipitation of ammonium selenites of varying composition. We are thus brought in contact with the experimental work of Cameron and Macallan (Proc. Roy. Soc., 1888, 44, 112), who obtained just such a precipitation by passing ammonia into a solution of selenion dioxide in absolute alcohol, the ammonia being described as having been carefully dried by passing it through a series of potash tubes; but the examination they made of their product and of a derivative of it led them to consider the two substances to be amidoselenites or selenosamates, and not merely selenites.

We have analysed and in other ways examined the products obtained in this way. The crystalline precipitate in presence of excess of ammonia is diammonium selenite, and can be rendered dry and anhydrous, without undergoing decomposition, in a potash desiccator charged with a strongly ammoniacal atmosphere. It is a very alkaline and very deliquescent salt, which yields up half its ammonia when its aqueous solution is distilled down to a small

volume; exposed in a sulphuric acid desiccator for 20 to 30 hours, it also loses half its ammonia, becoming the half-acid salt. Left for several months in such a desiccator, occasionally opened, it becomes the three-fourths acid selenite. The results of the analyses of the three salts were very satisfactory. They are given, as parts per 100, in the following table.

	$(NH_4)_2SeO_3$.	Found.	(NH ₄)HSeO ₃ .	Found.	$(NH_4)H_2(SeO_3)_2.$	Found.
SeO ₂	68.09	67.96	76.03	76.01	80· 73	81.51
NH.	20.87	21.02	11.64	10.88	6.18	6.22

It must be mentioned that the numbers for the selenion dioxide in the above two acid selenites differ very little, each to each, from those calculated for Cameron and Macallan's two selenosamates, whilst those for the ammonia differ greatly; as these chemists, however, adopted a method of questionable accuracy for determining the selenion, much stress cannot be laid upon this coincidence.

We have repeatedly, but fruitlessly, endeavoured to get these selenosamates, or any other salts which might be amido- or imidoselenites. Some years ago, also, Mr. Poyotaro Kamiya tried in this laboratory to prepare Cameron and Macallan's selenosamates, at the instigation of one of us, who then wanted to see whether the acid salt, $(NH_4)H(SeO_2NH_2)_2$, might not be really the diammonium imidoselenite, $HN(SeO_2NH_4)_2$. He failed, however, to get products of uniform composition, or any having the composition of Cameron and Macallan's salts, or any which did not readily yield up all their nitrogen as ammonia when boiled with potassium hydroxide. To Mr. Kamiya we are indebted for the preparation and analysis of the salt given above, which proved to be the three-fourths acid ammonium selenite.

We failed in our attempts to confirm the observation of Cameron and Macallan, that dry ammonia causes precipitation in a solution of selenious anhydride in absolute alcohol, having obtained, instead, only a very soluble salt, ethyl ammonium selenite; moreover, we found that a precipitation, apparently similar to theirs, was only obtained when moisture had in some way entered in, this precipitation consisting solely of ammonium selenites, showing the lack of trustworthy evidence in their paper for the existence of these salts.

The more acid ammonium selenite can be prepared from the normal or the less acid selenite by methods similar to those employed by Cameron and Macallan for obtaining the acid selenosamate from the normal selenosamate. No property of the selenosamates is recorded by which they are distinguishable from the acid selenites; it is, indeed, stated that a neutral solution gives hardly any precipitate with barium chloride until ammonia is added, but then that is equally

true of a neutral solution of ammonium selenite, the normal salt being strongly alkaline.

The only difficulty, but it is a great one, in the way of regarding the selenosamates as being merely selenites lies in the fact that the quantities of ammonia found in the two salts are just those corresponding with selenosamates and not with the selenites; this difficulty, we believe, is possibly due to the methods of analysis by which such results were obtained. In the first place, the normal selenosamate, described as continuously losing ammonia, was dried for analysis in a partial vacuum over sulphuric acid, and yet the proportions of both selenion dioxide and ammonia corresponded very closely indeed with the theoretical. Secondly, the selenion dioxide was estimated by passing chlorine into the solution of the selenosamate, and then precipitating as barium selenate; it was therefore estimated by a method which H. Rose, in 1861 (Ann. Phys. Chem., 113, 472; Zoit. anal. Chom., 1, 75), had condemned as being utterly untrustworthy, and which has again been discredited by Boutzoureano (Ann. Chim. Phys., 1889, [vi], 18, 296) as being far from giving accurate results. Lastly, Cameron and Macallan attempt to estimate the ammonia by direct distillation with alkali. and give no reason for not employing this method. Instead, they tried Kieldahl's nitrogen process, which they found to give excellent results with one selenosamate, but to be unsuitable for use in the analysis of the other; they offer no explanation of this marked difference, and we have to rely, without evidence, on the accuracy of the process in one case, although in the other precisely similar case it is found to be unsuitable. After failing, also, in the use of the sodalime process to determine the ammonia in the acid selenosamate. success was at last gained by using Dumas' nitrogen method. platinochloride method was tried with both salts, and gave indefinite results. It is certain that Cameron and Macallan, in some of their analyses of the acid selenosamate, got quantities of ammonia much below what they expected, thus favouring the supposition that this salt may have been the three-fourths-acid selenite. However that may be, we hold ourselves justified in asserting that there has not yet been any trustworthy evidence that selenion dioxide and ammonia in presence of alcohol or water give any other compounds than selenites. It may, therefore, be said of selenion dioxide that, unlike sulphur dioxide, it forms only oxylic salts, whether with alkyl radicles, with amines, or with metals.

LIV.—The Action of Certain Acidic Oxides on Salts of Hydroxy-acids. IV.

By George Gerald Henderson, D.Sc., M.A., Thomas Workman Orr, and Robert J. Gibson Whitehead.

In continuation of the investigations, the results of which have been already communicated to the Society (Henderson and Ewing, Trans., 1895, 67, 102; Henderson and Prentice, Trans., 1895, 67, 1030; Henderson and Barr, Trans., 1896, 69, 1451), we have now examined the action of the trioxides of molybdenum and tungsten, and of the dioxides of silicon, titanium, and tin on the primary alkali salts of the typical hydroxy-acids formerly selected for these experiments. It has been found that these oxides, with the single exception of silicic oxide, yield compounds with the hydroxy-acids similar to those which have already been described, and of which tartar emetic may be taken as the most familiar example; an account of the preparation and properties of these compounds follows.

Having now reached a point at which all our results may be conveniently summarised, we have drawn up the following list of all the compounds of the tartar emetic type of which the preparation has been recorded. It will be seen from this list that, whilst the existence of still more compounds of this nature appears to be possible—and we propose to examine this question in the near future—a number of substances have been obtained by the action of representatives of most of the groups of acidic oxides on salts of hydroxy-acids containing one or more alcoholic hydroxyl groups and one or more carboxyl groups, and that the study of these compounds renders it possible to draw conclusions regarding their constitution.

I.—Derivatives of lactic acid, CH₈·CH(OH)·COOH.

Boro-, arsenio-, and antimonio-lactates (Adam, Compt. rend., 1894, 118, 1274). Formulæ not given.

Molybdilactates, MoO₂(C₈H₄O₈M')₂.

II.—Derivatives of malic acid, COOH·CH, CH(OH)·COOH.

Boro-malates (Adam, Compt. rend., 1894, 118, 1274). Formulæ not given.

Antimoniomalates. Double salts,

 $2SbO(C_4H_4O_5M')_{22}SbO(C_4H_5O_5)_2$.

Molybdimalates. Two series, (a) $MoO_2(C_4H_4O_5M')_2$; (b) $MoO_2:C_4H_4O_5M'$.

Tungstimalates, WO2(C4H4O5M')2.

III. - Derivatives of citric acid,

 $COOH \cdot CH_2 \cdot C(OH) \cdot (COOH) \cdot CH_2 \cdot COOH$.

Borocitrates (Scheibe, Jahresberichte, 1879, 664). Two series, (a) BO·C₆H₆O₇M', and double salts, BO(C₆H₆O₇M'),BO(C₆H₇O₇);

(b) $(BO)_2C_6H_4O_7M'_2$.

Titanicitrates, TiO(C₆H₆O₇M')₂.

Stannicitrates, $SnO(C_6H_6O_7M')_2$.

Arseniocitrates. Double salts, AsO(C6H6O7M'), C6H6O7M'2.

Antimoniocitrates. Double salts, $SbO(C_6H_6O_7M')$, $C_6H_6O_7M'_2$; $SbO(C_6H_5O_7M'')$, $2C_6H_6O_7M''$; and also $SbO\cdot C_6H_7O_7$.

Molybdicitrates, $MoO_2(C_6H_6O_7M')_2$; $MoO_2(C_6H_6O_7)_2M''$.

Tungsticitrates. Double salts, $WO_2(C_6H_6O_7M')_2, C_6H_7O_7M'$; $2WO_2(C_6H_6O_7)_2M'', (C_6H_7O_7)_2M''$.

Tellurocitrates (Klein, Compt. rend., 1886, 102, 47), $TeO(C_6H_6O_7M')_9$.

IV.—Derivatives of tartaric acid, COOH (CH OH) COOH.

Borotartrates (Duve, Jahresb., 1869, 560). Two series, (a) $BO \cdot C_4 H_4 O_6 M'$; $BO \cdot C_4 H_8 O_6 M'_2$; $BO \cdot C_4 H_8 O_6 M''$; (b) $(BO)_2 C_4 H_8 O_6 M'$; $(BO)_2 C_4 H_2 O_6 M''$, and other more complex salts.

Titanitartrates, TiO(C₄H₄O₆M')₂, and TiO:C₄H₃O₆M'.

Stannitartrates, SnO(C₄H₄O₆M')₂, and SnO:C₄H₈O₆M'.

Arseniotartrates, $AsO \cdot C_4H_4O_6M'$; $(AsO \cdot C_4H_4O_6)_2M''$.

Arsenitartrates (Pelouze, Annalen, 1842, 44, 100), AsO2 · C4H4O6M'.

Antimoniotartrates, SbO·C₄H₄O₆M'; (SbO·C₄H₄O₆)₂M" SbO·C₄H₅O₆.

Molybditartrates, MoO₂(C₄H₄O₆M')₂.

Tungstitartrates, $WO_3(C_4H_4O_6M')_3$; $WO_3(C_4H_4O_6)_2M''$.

Tellurotartrates (Klein, Compt. rend., 1886, 102, 47), $TeO(C_4H_4O_6M')_2$; $TeO(C_4H_4O_6)_2M''$, and double salts, $TeO(C_4H_4O_6M')_2$, $2C_4H_5O_6M'$.

V.—Derivatives of mucic acid, COOH·(CH·OH)4·COOH.

Titanimucates, TiO:C₆H₇O₈M'.

Arseniomucates, AsO·C₆H₈O₈M'.

Antimoniomucates, $SbO \cdot C_6H_8O_8M'$, and double salts, $2(SbO \cdot C_6H_8O_8M')$, $C_6H_9O_8M'$.

Molybdimucates. Two series, (a) MoO_2 : $\text{C}_6\text{H}_7\text{O}_8\text{M}'$, and double salts, $2(\text{MoO}_2\cdot\text{C}_6\text{H}_7\text{O}_8\text{M}')$, $\text{C}_6\text{H}_9\text{O}_8\text{M}'$; (b) $(\text{MoO}_2)_2\text{C}_6\text{H}_5\text{O}_8\text{M}'$.

Tungstimucates, WO₂:C₆H₇O₈M'.

As regards the constitution of these compounds, in the first place it may be considered certain that they are not double salts in which the radicles (BO)', (SbO)', (MoO₂)", (TiO)", &c., play the part of metallic elements in replacing the hydrogen of one or more carboxyl groups.

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The presence of at least one alcoholic hydroxyl group in the acid is essential to the formation of compounds of the tartar emetic type; thus, for example, we found that no reaction occurred when arsenious and antimonious oxides were boiled with solutions of primary alkali Moreover, as is shown by the formulæ given succinates and oxalates. above, there is an obvious relation between the number of alcoholic hydroxyl groups in the molecule of the acid, the valency of the introduced radicle, and the composition of the new substance; for example, with lactic, malic, and citric acids, of which the molecule contains one alcoholic hydroxyl group, molybdenum trioxide forms compounds in which the bivalent (MoO_o) radicle is united to two molecules of the acid; with tartaric acid, which contains two alcoholic hydroxyl groups in its molecule, boric oxide forms two series of compounds, in which I molecule of the acid is united to one or two univalent (BO) radicles respectively; with mucic acid, which contains four alcoholic hydroxyl groups in its molecule, molybdenum trioxide forms two series of compounds in which I molecule of the acid is united to one or two bivalent (MoO_e) radicles repectively. over, as a general rule, the formation of these compounds (by the action of the oxides on boiling aqueous solutions of the primary alkali salts of the acids) proceeds more or less slowly, and reaches limits which depend largely on the concentration of the solutions, and on the relative masses of the interacting substances; in other words, the mode of formation has a far closer resemblance to the process of etherification than to the production of a metallic salt by the action of an acid on a basic oxide. It must also be noted that most of the salts are decomposed (hydrolysed) by water, to some extent at least.

The simplest view of the constitution of these compounds, which is in accordance with their mode of formation, composition, and properties, is that in them the radicles (BO), &c., replace the hydrogen of one or more alcoholic hydroxyl groups, giving rise to substances which may be compared with the acetyl, benzoyl, &c., derivatives of the hydroxy-acids. If this view is adopted, the following constitutional formulæ may be given to the acids, the salts of which have been prepared; it will be observed that, as a general rule, the free acids are more unstable than their salts, and that only a few of them have been isolated.

Molybdilactic acid, COOH CH COOH.

Antimoniomalic acid, COOH·CH₂·CH(O·SbO)·COOH.

Molybdi- and tungsti-malic acids,

COOH·CH₂·Ci-COOH and COOH·CH₂·CH-COO₂·O-M₀O₂·

Boro-, arsenio-, and antimonio-citric acids, $(COOH \cdot CH_2)_2C(O \cdot RO) \cdot COOH$ and $(COOH \cdot CH_2)_2C(O \cdot BO) \cdot COO(BO)$. Telluro-, titani-, and stanni-citric acids,

Molybdi- and tungsti-citric acids,

Boro-, arsenio-, and antimonio-tartaric acids, COOH·CH(OH)·CH(O·RO)·COOH and

Telluro-, titani-, and stanni-tartaric acids,

$$COOH \cdot CH \cdot O \cdot RO \cdot O \cdot CH \cdot COOH$$

Molybdi- and tungsti-tartaric acids,

Arsenitartaric acid, COOH·CH(OH)·CH(O·AsO₂)·COOH.

Arsenio- and antimonio-mucic acids,

$$COOH \cdot (CH \cdot OH)_8 \cdot CH(O \cdot RO) \cdot COOH.$$

Molybdi- and tungsti-mucic acids,

It is true that another view of the constitution of these compounds is justifiable in at least some cases. Thus Clarke (Amer. Chem. J., 1880, 2, 319) has adduced arguments in favour of regarding tartar emetic as the potassium salt of an unstable tartrantimonious acid, C4H4O6:Sb.OH. Similarly, the salts mentioned above might be regarded as derivatives of substituted boric, molybdic, titanic, and other acids; and, indeed, in the case of some of these, this at first sight appears to be a reasonable explanation of their constitution. Taking all circumstances into account, however, the formulæ which we have assigned to the salts seem on the whole preferable.

Apparently, few attempts have hitherto been made to prepare derivatives of aromatic hydroxy-acids analogous to tartar emetic and the numerous other salts which have now been obtained from hydroxy-acids of the aliphatic series. Salts of a borosalicylic acid have been described (Jahns, Jahresb., 1878, 760; Adam, Bull. Soc. Chim., 1894, [iii], 11, 204), but with this exception nothing has been

recorded, at least so far as we are aware. We have already shown (Trans., 1896, 69, 1454) that arsenious and antimonious oxides do not enter into reaction with alkali salts of salicylic, gallic, and mandelic acids—at any rate, under the conditions of our experiments—and it now remains to be seen whether other acidic oxides will behave similarly or not. This question we propose to investigate.

EXPERIMENTAL.

Molybdenum Trioxide and Primary Citrates.

Molybdicitrates of sodium, potassium, and ammonium were prepared by adding molybdenum trioxide (1 mol.), in small quantities at a time, to boiling aqueous solutions of the respective primary citrates (2 mols.). In each case, the oxide was dissolved very readily, and only a small portion of it was reduced. When dissolution of the oxide was complete, the solution was concentrated on the water-bath, and the crystals which separated on cooling were collected, drained at the filter pump, pressed between folds of filter paper, and analysed, with the following results.

Sodium molybdicitrate, $MoO_2(C_6H_6O_7Na)_2$. Found Mo = 17.57, calculated = 17.36 per cent.

Potassium molybdicitrate, $MoO_2(C_6H_6O_7K)_2 + 2H_2O$. Found Mo = 15.38, $H_2O + 6.09$; calculated Mo = 15.38; $H_2O = 6.39$ per cent.

Ammonium molybdicitrate, $MoO_2(C_6H_6O_7\cdot NH_4)_2 + \frac{1}{2}H_2O$. Found $Mo = 17\cdot 50$, $H_2O = 1\cdot 42$; calculated $Mo = 17\cdot 36$, $H_2O = 1\cdot 63$ per cent.

These three salts resemble each other closely. They form large, colourless, prismatic crystals, and are readily soluble in water, but insoluble in alcohol; they turn blue and decompose when heated at 100° , and also decompose very quickly when exposed to sunlight, and to some extent when exposed to diffused daylight, especially if in a moist state; their solutions show an acid reaction with litmus.

The corresponding barium salt, $MoO_3(C_6H_6O_7)_2Ba + 5H_2O$, was prepared by mixing concentrated solutions of the calculated quantities of the potassium salt and of barium chloride, and separated slowly

† In all cases, unless otherwise stated, the water of crystallisation was determined in a vacuum over sulphuric acid.

^{*} The following was found to be the best method of estimating molybdenum in these and similar compounds. An aqueous solution of the salt, made alkaline with ammonia and mixed with a large excess of yellow ammonium sulphide, is covered, left for 12 hours, and then acidified with dilute sulphuric acid. The precipitate which separates on standing is collected on a tared filter, washed, dried at 100°, and weighed; it is then separated from the filter paper as completely as possible, transferred to a tared crucible, weighed, ignited in a current of hydrogen at not too high a temperature, and weighed as MoS₂.

as a white, crystalline powder, which, when once deposited from solution, is almost insoluble in water. Washed with cold water and dried in air, it gave the following figures on analysis.

Mo = 13.67, Ba = 18.44, $H_2O = 12.78$; calculated Mo = 13.06, Ba = 18.65, $H_2O = 12.25$ per cent.

With the object of obtaining molybdicitric acid, $MoO_9(C_6H_7O_7)_9$, the barium salt, finely powdered, was suspended in water and decomposed by the addition of slightly less than the calculated quantity of sulphuric acid. After removing the precipitated barium sulphate, a clear, colourless solution was left, which contained a soluble compound of molybdenum and had a strongly acid reaction, although quite free from sulphuric acid. This solution remained for several months without undergoing any change; when it was concentrated in a vacuum desiccator, a yellowish, gelatinous solid separated, which could not be induced to crystallise, but gradually became blue and decomposed. Thus, although the acid was not isolated in a crystalline state, there is little doubt that it was present in the solution.

Attempts were also made to prepare derivatives of citric acid containing proportions of molybdenum different from those in the salts described above, but although a solid substance, in which the percentage of molybdenum was considerably greater, was obtained, it could not be said with certainty that this was a definite compound.

Tungsten Trioxide and Primary Citrates.

Tungsten trioxide, like molybdenum trioxide, was dissolved by boiling aqueous solutions of primary alkali citrates, but the compounds produced were shown by analysis to be double salts, composed of 1 mol. of tungsticitrate combined with 1 mol. of alkali citrate, and simple tungsticitrates analogous to the molybdicitrates could not be obtained by this method. In preparing these compounds, the oxide was added in small quantities at a time to the solution of the citrate until no more was dissolved; the solution was then filtered, evaporated to a syrupy consistency on the water-bath, and left to stand. As a rule, crystallisation only began after some time, and proceeded slowly. The salts were purified by recrystallisation from water, the crystals being washed with a little cold water, then with alcohol, and dried between folds of filter paper. The following double salts were prepared in this manner:

Sodium tungsticitrate, $WO_2(C_6H_6O_7Na)_2, C_6H_7O_7Na + \frac{1}{2}H_2O$. Found $W = 22\cdot10$, $H_2O = 1\cdot08$; calculated $W = 22\cdot19$, $H_2O = 1\cdot09$ per cent.

Potassium tringsticitrate, $WO_2(C_6H_6O_7K)_2$, $C_6H_7O_7K + 3\frac{1}{2}H_2O$. Found W = 19.51, $H_2O = 6.74$; calculated W = 19.80, $H_2O = 6.73$ per cent.

Ammonium tungsticitrate, $WO_2(C_6H_6O_7\cdot NH_4)_2$, $C_6H_7O_7\cdot NH_4 + 2H_2O$. Found $H_9O = 4\cdot28$; calculated = 4·10 per cent.

These salts crystallise in small, colourless prisms, very easily soluble in water, but insoluble in alcohol. The sodium and potassium salts can be heated to about 120° without being decomposed, but the ammonium salt is somewhat less stable; their solutions show an acid reaction with litmus, and the addition of mineral acids or alkalis causes decomposition.

The double barium salt, $2WO_2(C_6H_6O_7)_2Ba,(C_6H_7O_7)_2Ba+10H_2O$, was obtained by mixing concentrated aqueous solutions of the potassium salt and of barium chloride, and leaving the solution to evaporate in a vacuum desiccator. The crystals which separated were purified by recrystallisation from water, and the salt was thus obtained in the form of minute, colourless needles. It is easily soluble in water, and more stable in solution than the alkali salts, to which it was shown by analysis to be similar in composition.

Found W=17.47, Ba=19.35, $H_9O=8.81$; calculated W=17.62, Ba=19.58, $H_9O=8.57$ per cent.

Molybdenum Trioxide and Primary Malates.

The molybdimalates of sodium, potassium, and ammonium were prepared in the same way as the corresponding molybdicitrates. Molybdenum trioxide (1 mol.) was dissolved readily by boiling solutions of the primary malates (2 mols.) without undergoing reduction, and the compounds produced, which separated in a crystalline form when the solutions were concentrated, were purified by recrystallisation from water.

The sodium salt, $MoO_2(C_4H_4O_5Na)_2 + 3H_2O$, which forms small, colourless, prismatic crystals, is easily soluble in water, but insoluble in alcohol; the solution gives an acid reaction with litmus. It is decomposed, turning blue, when heated at about 100° , and it is also sensitive to light, behaving in the same way as when heated. Analysis of the air-dried salt gave the following figures. Found Mo = 19.37, $H_2O = 10.45$; calculated Mo = 19.31, $H_2O = 10.97$ per cent.

The potassium salt, $MoO_2(C_4H_4O_5K)_2 + 2H_2O$, crystallises in large, colourless flat prisms, but in other respects closely resembles the sodium salt. Found $Mo = 19\cdot23$, $H_2O = 7\cdot62$; calculated $Mo = 18\cdot99$, $H_2O = 7\cdot11$ per cent.

The ammonium salt, MoO₂(C₄H₄O₅·NH₄)₂, was much more difficult to purify than the others, and required repeated crystallisation from water. It is a white, crystalline powder, soluble in water, decomposed by heating at 100°, and much more sensitive to light than the salts of

the alkali metals. As is seen from the analytical results, it crystallises in the anhydrous state. Mo found = 22.31; calculated = 22.46 per cent.

When concentrated solutions of barium chloride and of sodium molybdimalate were mixed, a white solid was slowly precipitated; this was found to contain Mo = 22.41, Ba = 24.59, and $H_0O = 7.88$ per cent., but its composition does not agree with that calculated for a barium molybdimalate analogous to the other salts described. insoluble in water.

Another molybdimalate of quite different constitution was prepared by gradually adding molybdenum trioxide to a boiling aqueous solution of primary sodium malate until no more of the oxide was dissolved; the solution was then concentrated on the water-bath, cooled, and mixed with alcohol, a viscous liquid being precipitated, which gradually solidified when left in contact with the mother liquor. The crystalline solid was separated and purified by repeated solution in water and precipitation with alcohol, until its composition remained constant. Analysis of the air-dried salt showed it to be a sodium molubdimalate of the formula $MoO_o: C_{\downarrow}H_oO_{z}Na + 1\frac{1}{2}H_oO$. Found $Mo = 31\cdot29, H_oO = 8\cdot93$; calculated Mo = 31.07, $H_2O = 8.73$ per cent. This salt crystallises from dilute alcohol in long colourless needles; it is easily soluble in water, and is very sensitive to light, quickly turning blue when exposed to diffused daylight. It is also decomposed by heating at about 90°.

From this it is seen that two distinct classes of molybdimalates are capable of existence.

Tungsten Trioxide and Primary Malates.

Tungsten trioxide was found to dissolve very slowly in aqueous solutions of primary alkali malates, and even after prolonged boiling considerable quantities of unchanged malates remained in the solutions; these were separated from the tungstimalates which had been . formed, by fractional precipitation with alcohol, after concentrating the solutions on the water-bath. The first fractions which were thrown down consisted mainly of the less soluble malates; the last comprised the more soluble new compounds, which were finally purified by repeated crystallisations from dilute alcohol until their composition was constant.

Sodium tungstimalate, WO₂(C₄H₄O₅Na)₂, which crystallises from dilute alcohol in small white needles containing 34.98 per cent. of tungsten (calculated = 35.11), is easily soluble in water, but only sparingly in dilute alcohol, and is not decomposed by exposure to a temperature of 105°,

The potassium salt, $WO_2(C_4H_4O_5K)_2$, was much more difficult to purify, as its solubility in dilute alcohol does not differ much from that of potassium hydrogen malate. It crystallises in long needles, is readily soluble in water, and is not easily decomposed by heat. Found $W=31\cdot27$, calculated $=33\cdot09$ per cent.

The ammonium salt, $WO_2(C_4H_4O_5\cdot NH_4)_2 + \frac{1}{2}H_2O$, crystallises in small, light leaflets; it is also readily soluble in water, and can be heated, at 105° without decomposition. Found $W=34\cdot 35$, $H_2O=2\cdot 34$; calculated $W=35\cdot 14$, $H_2O=1\cdot 71$ per cent.

The solutions of these salts give an acid reaction with litmus.

Molybdenum Trioxide and Primary Mucates.

Molybdenum trioxide (1 mol.), added in small instalments to a boiling aqueous solution of primary potassium mucate (2 mols.), was readily dissolved, only a small part of the oxide being reduced. first crops of crystals obtained on concentrating the solution consisted, for the most part, of unaltered mucate, but finally a solid was isolated which, after being washed with a little cold water and dried between folds of filter paper, gave, on analysis, Mo = 13.88 and H_oO = 19.83 per cent. A double molybdimucate of potassium of the formula $2(M_0O_0:C_6H_7O_8K),C_6H_9O_8K+16H_9O$ would contain $M_0=14.86$ and $H_2O = 22.41$ per cent. Our salt lost only $14H_2O$ in a vacuum over sulphuric acid (calculated = 19.61 per cent.); its formula might written, $2[M_0O_2(OH)\cdot C_0H_2O_8K], C_0H_2O_8K + 14H_2O.$ therefore be It is a finely crystalline powder, usually more or less coloured by traces of brown impurities, and sparingly soluble in water. When heated, it turns brown and decomposes. It is also unstable in solution, for when it was dissolved in water, with the object of purifying it by recrystallisation, the solution deposited indistinct crystals containing a higher percentage of molybdenum, whilst at the same time amorphous, brown decomposition products were formed which, although soluble in water, prevented the crystallisation of the molybdimucate. These impurities were removed by the cautious addition of alcohol to the solution until, by precipitation of a sticky brown mass, the liquid was rendered almost colourless; after filtration, more alcohol was added to the solution and an almost colourless syrup was precipitated which became crystalline when left for some time in contact with the The solid was collected, washed with dilute alcohol, pressed between folds of filter paper, and, on analysis, proved to be potassium molybdimucate, MoOo:CoH,OoK+5HoO. Found Mo=19.85, $H_2O = 15.99$; calculated $M_0 = 20.56$; $H_2O = 19.37$ per cent. vacuum, the salt loses only 4H₂O (calculated = 15.49 per cent.) and hence the formula $(M_0O_2 \cdot OH)C_6H_8O_8K + 4H_2O$ might be assigned to it.

This salt is a white, crystalline powder, fairly easily soluble in water, but only sparingly in dilute alcohol, and is decomposed by exposure to a temperature of 90-95°. When in the dry state, it is fairly stable towards light, but in solution it gradually decomposes even in the dark, and quickly on exposure to light, forming soluble, brown, amorphous products.

A double ammonium salt was also prepared. When the solution obtained by boiling molybdenum trioxide with primary ammonium mucate was submitted to fractional crystallisation, it finally deposited a solid which, after being dried in air, gave, on analysis, Mo = 17.59, $H_2O = 12.92$. The formula $2(M_0O_2: C_6H_7O_8: NH_4), C_6H_9O_8: NH_4 + 10H_2O_8: NH_4 + 10H_4O_8: NH_4O_8: NH_4 + 10H_4O_8: NH_4O_8: requires Mo = 17.14 and $H_oO = 16.15$ per cent., so that in a vacuum the salt lost only 8H₂O (calculated = 12.92), and its formula may be $2[M_0O_2(OH)\cdot C_6H_3O_8\cdot NH_4], C_6H_9O_8\cdot NH_4 + 8H_2O$. This salt is a white powder, very easily soluble in water, and decomposed by heat. The addition of alcohol to an aqueous solution of the salt causes the precipitation of a colourless syrup which gradually solidifies when left in contact with the liquid, but this solid, as analysis showed, is the simple ammonium molybdimucate, MoO2: C6H7O8: NH4+5H2O, and not the double salt. Found Mo = 20.98, calculated = 21.53 per cent., $H_2O = 15.75$, the formula requiring $H_2O = 20.02$ per cent., hence the salt loses only 4H₂O in a vacuum (calculated = 16.01) and a possible ormula for it is MoO₂(OH)·C₆H₈O₈·NH₄ + 4H₂O.

Ammonium molybdimucate is a white, crystalline powder readily soluble in water but only sparingly in dilute alcohol. Its behaviour towards heat and light is similar to that of the potassium salt, and it also slowly decomposes in aqueous solution, forming brown products.

The double sodium salt was obtained in a similar manner, although not quite free from brown impurities, owing to its greater instability. Analysis gave Mo = 18.92 and $H_2O = 2.32$. The formula $2(M_0O_0: C_0H_2O_0N_8), C_0H_0O_0N_8 + 3\frac{1}{2}H_2O$ requires $M_0 = 18.87$ $H_2O = 6.22$ per cent.; thus, in a vacuum, the salt loses only $1\frac{1}{2}H_2O$ (calculated = 2.66), and its composition may be expressed by the formula: $2[MoO_2(OH)\cdot C_6H_8O_8Na], C_6H_9O_8Na + 1\frac{1}{2}H_2O.$

As already stated, the crystalline powder, in which form the salt was prepared, was discoloured by traces of impurities; it formed a brown solution in water, and this, when concentrated, dried up to a horny mass without crystallising. Alcohol was added to the solution in the expectation that the impurities would be thrown down first, but in this case the method was unsuccessful. Nothing was obtained but a dark brown, viscous liquid, which, when separated from the mother liquor, dried up to an amorphous mass containing abundance of molybdenum, but from which no crystalline substance could be prepared. Digitized by Google

All the molybdimucates described are more or less deliquescent when in an anhydrous state.

Observation of the ease with which molybdenum trioxide is dissolved by solutions of alkali mucates led us to institute experiments with the object of ascertaining whether compounds containing a higher percentage of molybdenum than those already described were capable of existence, and as a result we succeeded in preparing representatives of another series of molybdimucates of the formula $(MoO_0)_0C_0H_5O_0M'$ or $(MoO_0\cdot OH)_0C_0H_7O_0M'$.

To boiling aqueous solutions of the primary mucates of sodium, potassium, or ammonium, molybdenum trioxide was added in small quantities at a time until no more would dissolve, this point being reached when the substances were present in approximately molecular proportion; in each case, dissolution went on quickly, and but little of the oxide was reduced. The solutions, when concentrated on the water-bath and left, deposited fine powders, which closely resembled the mucates in appearance.

Potassium dimolybdimucate, $(MoO_2)_2C_6H_5O_8K+6\frac{1}{2}H_2O$, when repeatedly crystallised from water until constant in composition, and dried in air, was found to contain $Mo=31\cdot09$; $H_2O=12\cdot65$. The formula requires $Mo=31\cdot01$; $H_2O=18\cdot99$ per cent.; so that in a vacuum the salt loses only $4\frac{1}{2}H_2O$ (calculated = $13\cdot15$), and therefore the formula $(MoO_2\cdot OH)_2C_6H_7O_8K+4\frac{1}{2}H_2O$ might be given to it. This salt is a white powder very sparingly soluble in rold, but fairly easily in hot water. When moist, it is very sensitive to light, turning blue even when screened from direct daylight, but when dry it is not affected. It is decomposed by heat, turning brown below 100° . When its solution is heated for a time, it turns blue, owing to slow decomposition of the salt.

Considerable difficulty was experienced in purifying sodium dimolybdimucate, $(MoO_2)_2C_6H_5O_8Na+6\frac{1}{2}H_2O$, owing to the ease with which it decomposes when its solution is heated for any length of time, and also to the fact that its solubility is much the same as that of primary sodium mucate. In properties, it closely resembles the potassium salt, and its composition is similar. The air-dried salt gave $Mo=31\cdot02$ and $H_2O=12\cdot23$, but the formula requires $Mo=31\cdot71$ and $H_2O=18\cdot16$ per cent.; hence, in a vacuum, the salt only loses $4\frac{1}{2}H_2O$ (calculated = $12\cdot58$), and its formula might be written $(MoO_0\cdotOH)_0C_0H_7O_2Na+4\frac{1}{2}H_2O$.

The ammonium salt is more easily purified than the others, because it is considerably less soluble in water than ammonium hydrogen mucate, and does not decompose readily when its aqueous solution is heated. It separates as a soft, white powder, and its properties are very similar to those of the potassium salt. Analysis showed its formula

to be $(MoO_2)_{22}C_8H_5O_8\cdot NH_4 + 7H_2O$. Found Mo = 31.85, $H_2O = 14.82$, the formula requiring Mo = 32.12, and H₂O = 21.21 per cent.; the salt thus loses only 5H₀O (calculated = 15.15) in a vacuum, and its formula may be $(MoO_2 \cdot OH)_2$, $C_6H_7O_8 \cdot NH_4 + 5H_2O$.

All these salts, when rendered anhydrous, are somewhat hygroscopic.

Tungsten Trioxide and Primary Mucates.

It was found that a boiling aqueous solution of primary potassium mucate dissolved tungsten trioxide, although very slowly. After prolonged heating, with repeated addition of small quantities of the oxide so as to have some undissolved oxide always present, the solution was filtered and concentrated; unchanged mucate separated first, and ultimately a thick liquid was left which showed no signs of crystallising, and was therefore mixed with alcohol. In this way, a syrupy precipitate was formed, which gradually solidified when left in contact with the liquid. The solid thus obtained was purified by repeatedly dissolving it in water and precipitating with alcohol; it was always thrown down as a viscid liquid, or in a semi-solid state, and showed a tendency to retain that form for a considerable period; if placed on a porous tile when in this condition, it dried up to a horny mass, but when left it slowly became crystalline. The purified solid was shown on analysis to be potassium tungstimucate, $WO_3: C_6H_7O_8K + 3H_2O$. Found W = 34.67, $H_0O = 11.06$; calculated W = 35.66, $H_0O = 10.47$ per cent.; the water of crystallisation was determined at 100°. It will be observed that there is apparently no formation of a double salt in the first instance, as is the case with the molybdimucates.

Potassium tungstimucate is obtained in the form of a white, crystalline solid, which is composed of a mass of very minute, lustrous crystals; it is very readily soluble in water and fairly in dilute alcohol. It is more stable than the corresponding molybdenum compound, and can be heated to 100°, or exposed to light, without decomposition.

The formation and purification of this salt occupied so much time that we did not prepare any other tungstimucate.

Molybdenum Trioxide and Lactates.

It has already been stated in a former communication (Henderson and Prentice, loc. cit.) that arsenious and antimonious oxides dissolve in solutions of alkali lactates, but that, whilst the syrupy products which we obtained were found to contain arsenic and antimony respectively, no definite compounds were isolated in a purified state. In view of the fact that the compounds formed by the action of molybdenum trioxide on the salts of the other hydroxy-acids investigated generally crystallise well, we were encouraged to attempt the preparation of a crystalline molybdilactate, as it was desirable to obtain a definite derivative of lactic acid. In this case, our efforts met with success.

Molybdenum trioxide (1 mol.) was added in small quantities at a time to a boiling concentrated aqueous solution of potassium lactate (2 mols.); the oxide was readily dissolved, but at the same time some of it was reduced, and the solution acquired a blue colour. The solution was concentrated to small bulk on the water-bath, and after being left for a long time, a small quantity of a solid crystallised out: this was collected, drained on a porous plate, and analysed. It proved to be potassium molybdilactate, $\text{MoO}_2(\text{C}_3\text{H}_4\text{O}_3\text{K})_2$. Found Mo = 24.28; calculated = 25.00 per cent.

This salt forms small, colourless crystals, which are very readily soluble both in water and in dilute alcohol. When dry, it is not very sensitive to light, but is decomposed by exposure to a temperature of 90°. The addition of alcohol to the mother liquor, from which the crystals had separated, caused the precipitation of a colourless syrup which rapidly turned blue, but did not solidify even after prolonged contact with the liquid, or exposure to the air.

A boiling aqueous solution of sodium lactate dissolved molybdenum trioxide readily, but sodium molybdilactate has not yet been obtained in a crystalline form. A solution of barium lactate also dissolved the oxide of molybdenum, but no crystalline barium salt could be isolated.

From the remaining acidic oxides not already examined by us, we selected the dioxides of silicon, titanium, and tin, and studied their action on primary alkali salts of the hydroxy-acids mentioned below. Compounds of the last two oxides were prepared, and are described in what follows, but silicon dioxide, even in the hydrated state, was found to be almost, if not altogether, insoluble in boiling solutions of all the salts examined, and it would seem that if analogous silicon compounds are capable of existence they must be prepared in a different manner.

Titanium Dioxide and Primary Tartrates.

The titanitartrates of sodium, potassium, and ammonium were prepared by adding hydrated titanium dioxide * (1 mol.) in small quantities at a time to boiling aqueous solutions of the respective primary tartrates (2 mols.); dissolution took place very slowly, but after

* Hydrated titanium dioxide was used in all our experiments, because the anhydrous oxide was found to be almost insoluble in solutions of the salts which we used.

prolonged boiling the greater part of the oxide was dissolved. The solutions were then filtered, and evaporated to crystallisation on the water-bath; the first crops of crystals which separated consisted principally of unchanged tartrates, but finally the more soluble titanitartrates crystallised in a fairly pure state. The sodium and potassium salts were obtained in a state of purity by dissolution in water and precipitation with alcohol, several times repeated, whilst the ammonium salt was best purified by recrystallising it from water until its composition remained constant. The following results were obtained on analysing the air-dried salts, the water of crystallisation being determined in each case at 105°.

Sodium titanitartrate, $TiO(C_4H_4O_6Na)_2 + 8H_2O$. Found Ti = 8.88, $H_2O = 26.41$; calculated Ti = 8.74, $H_2O = 26.18$ per cent.

Potassium titanitartrate, $TiO(C_4H_4O_6K)_2 + 4\frac{1}{2}H_2O$. Found Ti = 9.21, $H_2O = 15.44$; calculated Ti = 9.24, $H_2O = 15.60$ per cent.

Ammonium titanitartrate, $TiO(C_4H_4O_6\cdot NH_4)_2 + 3\frac{1}{2}H_2O$. Found Ti = 9.82, $H_2O = 13.96$; calculated Ti = 10.45, $H_2O = 13.72$ per cent.

These salts crystallise in small, colourless prisms, readily soluble in water, but almost insoluble in alcohol. They are quite stable, and can be heated above 100° without decomposing, and their solutions can be heated for some time, after the addition of mineral acids or alkali, without undergoing any visible change. The sodium and potassium salts are precipitated unchanged from their aqueous solutions on adding alcohol, but the ammonium salt appears to be partly decomposed under these circumstances, the crystalline solid which is then precipitated containing a much higher percentage of titanium than the original salt. Its composition corresponds more nearly with that required for the formula TiO:C₄H₃O₆·NH₄, and possibly it is a representative of another series of titanitartrates.

When concentrated solutions of the potassium salt and of barium chloride are mixed, a white precipitate of the barium salt is at once thrown down as a white powder, almost insoluble in cold, and only sparingly soluble in hot water; it can be heated to 120° without decomposition. Its composition agrees fairly well with the formula $TiO(C_4H_4O_6)_9Ba + 5H_9O$.

Tin Dioxide and Primary Tartrates.

It was found that hydrated stannic oxide * (1 mol.) was dissolved very slowly by boiling aqueous solutions of primary alkali tartrates (2 mols.), although more readily than titanic oxide; when the

[•] Anhydrous stannic oxide is practically insoluble in solutions of all the salts we examined.

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filtered solutions were concentrated, unaltered tartrates crystallised first, and the more soluble stannitartrates last. The sodium salt was purified by dissolving it in water and precipitating with alcohol, the potassium and ammonium salts by crystallisation from water, repeated in each case until the composition remained constant. Analysis of the air-dried salts gave the following results, the water of crystallisation being determined in each case at 105°.

Sodium stannitartrate, $SnO(C_4H_4O_6Na)_2 + 6H_2O$. Found $Sn = 20\cdot12$, $H_2O = 18\cdot03$; calculated $SnO = 20\cdot20$, $H_2O = 18\cdot40$ per cent. Potassium stannitartrate, $SnO(C_4H_4O_6K)_2 + 2H_2O$. Found $Sn = 20\cdot20$

21.88, $H_2O = 6.47$; calculated Sn = 21.70, $H_2O = 6.61$ per cent.

Ammonium stannitartrats, $SnO(C_4H_4O_6\cdot NH_4)_2 + 1\frac{1}{2}H_2O$. Found $Sn = 25\cdot 69$, $H_2O = 5\cdot 30$; calculated $Sn = 25\cdot 96$, $H_2O = 5\cdot 47$ per cent.

The salts crystallise in small, colourless prisms, and are fairly easily soluble in water, but are decomposed to some extent by prolonged heating of their aqueous solutions; they are also decomposed on adding acid or alkali to the hot solution. In the dry state, they are quite stable, and can be heated above 100° without undergoing any change other than loss of water of crystallisation. The sodium salt is precipitated unchanged when alcohol is added to its solution in water, but the potassium and ammonium salts are to some extent altered, as the crystalline solids which are precipitated by alcohol contain a much higher percentage of tin than the original salts, and agree fairly well in composition with the formula SnO:C₄H₃O₆M'; in this respect, they resemble ammonium titanitartrate. It appears, therefore, that a second series of stannitartrates is capable of existence.

A white precipitate is formed at once when concentrated solutions of sodium stannitartrate and barium chloride are mixed; this, when dry, is a white powder, almost insoluble in hot water, and can be heated above 100° without decomposition. Its composition agrees pretty closely with that calculated for barium stannitartrate, $\operatorname{SnO}(C_4H_4O_6)_2\operatorname{Ba} + 4\frac{1}{2}H_3O$.

Titanium and Tin Dioxides and Primary Citrates.

Potassium titanicitrate, $TiO(C_6H_6O_7K)_2 + H_2O$, and ammonium stannicitrate, $SnO(C_6H_6O_7\cdot NH_4)_2 + \frac{1}{2}H_2O$, were obtained by dissolving the hydrated dioxides in boiling aqueous solutions of the corresponding primary citrates; the process is a very slow one, especially in the case of titanium dioxide, and considerable decomposition of the citrates takes place. When the filtered solutions were concentrated, some unchanged citrate separated, and after removal of this the new salts were precipitated by addition of alcohol. They were freed from

admixed citrate by repeated solution in water and fractional precipitation with alcohol, being less soluble in dilute alcohol than the citrates, and the air-dried salts were analysed with the following results. Titanicitrate: Found Ti = 8.42, $H_2O = 4.17$; calculated Ti = 8.89, $H_2O = 3.33$ per cent. Stannieitrate: Found Sn = 21.91. $H_9O = 1.43$; calculated Sn = 21.11, $H_9O = 1.61$ per cent.

From an aqueous solution, the titanicitrate is thrown down by alcohol in small, white crystals, and the stannicitrate as a syrupy liquid, which dries up to a white mass when exposed in a desiccator over sulphuric acid. The stannicitrate can be obtained in small, white crystals from dilute alcohol by adding ether to the solution. Both salts are very readily soluble in water, and are also soluble in dilute alcohol. They are not decomposed at 100°, and are not notably sensitive to light, but their aqueous solutions gradually turn brown if boiled for any length of time.

Titanium and Tin Dioxides and Primary Malates.

Hydrated titanium dioxide dissolved very slowly in a boiling aqueous solution of primary potassium malate, and on adding alcohol to the solution, a syrupy liquid was precipitated, which, when re-dissolved in water, was reprecipitated by alcohol as a white powder; this, however, proved to be a mixture of potassium titanate and malate, and not a definite compound. Hydrated stannic oxide dissolved in the solution of the malate more readily than titanic oxide, and the addition of alcohol to the solution caused the precipitation of a gelatinous solid. After repeated dissolution in water and precipitation with alcohol, the composition of the solid agreed closely with that calculated for a substance of the formula C4H5O5K,H10Sn5O15, but it cannot be stated with certainty that this is a definite compound.

Titanium and Tin Dioxides and Primary Mucates.

A boiling solution of primary potassium mucate was found to dissolve hydrated titanium dioxide, but only very slowly, and a considerable portion of the mucate was decomposed into soluble, brown, amorphous products. The solution, after removing the excess of oxide, was mixed with alcohol, when the new compound separated in the solid form, leaving a great part of the impurities in solution; it was purified by a repetition of this process, and was then shown by analysis to be potassium titanimucate, TiO:C₆H₇O₈K + 3H₂O. Found Ti = 12.78, $H_0O = 14.71$; calculated Ti = 13.19, $H_0O = 14.81$ per cent.

The salt forms small, white crystals, which are very easily soluble Digitized by GOOGLE VOL. LXXV.

in water, but only sparingly so in dilute alcohol. It is not sensitive to light, and can be heated to 100° without decomposition.

Attempts to prepare a corresponding compound of tin were unsuccessful.

We are indebted to Mr. W. S. Denham for valuable assistance in part of this work..

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LV.—Derivatives of aa'-Dibromocamphorsulphonic Acid.

By ARTHUR LAPWORTH.

The substitution derivatives of camphor which have hitherto been obtained are of at least three distinct types. In the commonest type, the representatives of which are known as a-derivatives, the substituent replaces a hydrogen atom of the -CH₂·CO- group, and both mono- and di-derivatives of this class are known; they are produced by the action of chlorine and bromine at fairly low temperatures, by nitration of a-mono-derivatives, by the action of sodium and alkyl iodides, and, in general, in those cases where substitution is known to occur in the a-position in other ketones. Lowry has shown (Trans., 1898, '73, 569) that the ordinary a-dihalogen derivatives of camphor contain both halogen atoms in this position, and has suggested that the substituent in this position be termed a- or a'-, according to its space orientation with regard to the camphor nucleus.

A second position in the camphor nucleus is sometimes liable to attack; the hydrogen at this point, known as the β -position, appears, however, to be replaced only through the occurrence of isomeric change in an α -brominated derivative, under the influence of hydrogen bromide. The new position occupied by the bromine atom in these derivatives is not known; it may, however, be mentioned that a similar migration of a bromine atom in an α -brominated ketone has been noticed by Conrad and Schmidt, who found that when bromine is added to ethylic acetoacetate dissolved in carbon bisulphide, the amount of γ -bromo-derivative, CHBr·CO·CH₂·COOEt, produced depended solely on the length of time the initial product,

CH₈·CO·CHBr·COOEt,

remained in contact with the hydrogen bromide produced in the reaction (*Ber.*, 1896, 29, 1042). If, then, the change of aa'-dibromocamphor into $a\beta$ -dibromocamphor is of a similar nature, the latter would be represented as containing the group :CBr·CO·CHBr·, as

Tiemann has suggested, in explanation of its transformation into campholenic acid under the influence of sodium amalgam.

A third series of derivatives, known as the π -derivatives, is obtained indirectly from the corresponding sulphonic acids which are produced when camphor and its α -halogen derivatives are treated with an excess of sulphuric or chlorosulphonic acid. These appear to contain the substituent in a methyl group (Kipping, Trans., 1896, 69, 920), and may, therefore, be represented by the general formula

$$X \cdot CH_2 \cdot C_7H_{11} < \stackrel{CH_2}{\leftarrow}$$

To these may possibly be added a new type, represented at present by the newly discovered sulphonic derivatives produced by treating camphor with a mixture of sulphuric and acetic anhydride (Reychler, Bull. Soc. Chim., 1898, [iii], 19, 120); these are not identical with the π -derivatives, but may possibly be α - or β -derivatives. So far, however, no evidence as to their constitution has been adduced.

The sulphonic group, being of an "unsaturated" type similar to that of the carboxyl group, might be expected, under favourable conditions, to render the hydrogen of the contiguous carbon atom replaceable by substituents; this also appeared probable from the fact that, in the aromatic series, the sulphonic group renders the "meta" hydrogen atom directly replaceable, thus being brought into line with those groups which, in the fatty series, lead to the production of a-sub-It seemed not impossible, therefore, that, by stitution derivatives. bromination of a-bromocamphor-x-sulphonic acid, a dibrominated acid containing the group :CBr·SO.H might be produced, and the investigation of the compound could hardly fail to afford further evidence as to the true position of the sulphonic group in the camphor nucleus. the other hand, it was equally likely that the substitution might take place in the a-position, giving a sulphonic acid of ordinary aa'-dibromocamphor, or in the β -position giving an acid derived from $\alpha\beta$ -dibromocamphor. The question was therefore one of considerable interest, and the present paper contains an account of certain derivatives of the acid in question, and of the methods employed for determining its constitution.

The dibromo-acid was first obtained by Dr. Kipping and the author (Trans., 1897, 71, 19) by acting on a-bromocamphorsulphonic acid with dilute nitric acid, the additional bromine atom having been supplied by the destruction of the larger portion of the monobromo-acid. Its true nature, however, was not at first recognised, and the substance was thought to be hydroxydibromocamphorsulphonic acid, $C_{10}H_{14}Br_2SO_5$; this formula, as we have since shown (Proc., 1898, 14, 159), should in reality be $C_{10}H_{14}Br_2SO_4 + H_2O$.

The method of preparation, however, left much to be desired, as at

least half the original substance is broken down, and the difficulty of isolating the dibromo-acid was increased by the presence of large quantities of oxidation products. Experiments were therefore made with the object of ascertaining if the substance could not be prepared by the direct action of bromine on the monobromo-acid. It was found that, whilst the dry ammonium salt was but slowly attacked by bromine when heated with it in open vessels at temperatures below 100° , a nearly quantitative yield of the dibromo-derivative could be obtained by heating an aqueous solution of the salt with the calculated amount of bromine in sealed tubes at 100° , this method being used throughout.

Having obtained in this manner fairly large quantities of the dibromo-acid, its properties were studied more closely than was previously possible. Its salts were found to be well defined substances as a rule, and in the case of the barium and lead salts, were less soluble than those of the monobromo-acid; the basic lead salt is practically insoluble, whereas that of the monobromo-acid is readily soluble in cold water.

A number of new derivatives have also been examined, including the sulphonic chloride, amide, and piperidide; these, like the sulphonic bromide previously described, may readily be obtained in large crystals. The sulphonic chloride resembles closely in appearance, crystalline form, and mode of development, the sulphonic bromide, and the axial ratios of the two substances are not widely different; both compounds, as well as the sulphonic amide, belong to the orthorhombic system and exhibit the phenomenon of sphenoidal hemihedrism.

In the former paper, it was also shown that, by boiling the aqueous solution of the acid with silver nitrate and evaporating the filtered liquid to dryness, a neutral substance having the formula $C_{10}H_{12}Br_2SO_4$, may be obtained; as this is not formed when alkali is used, much attention was paid to the question of the action of alkalis on the various derivatives of the dibromo-acid, and it was found that they exert a reducing influence, producing derivatives of a-monobromocamphorsulphonic acid. This mode of action of aqueous alkali is not often met with in other series, but is very characteristic of the aa'-di-derivatives of camphor; thus, the aa'-di-halogen compounds, and aa'-bromo- or -chloro-nitrocamphors lose halogen readily under the influence of caustic potash or soda, being reduced to the corresponding a-mono-derivatives.

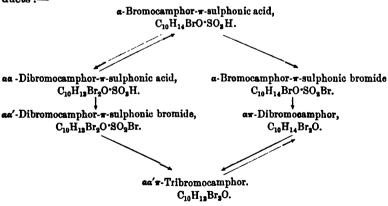
The action of piperidine on the sulphonic chloride is somewhat curious; when the action was restrained by the presence of ether as a diluent, the product, although at first insoluble in cold water, gradually dissolved in it; moreover, a considerable proportion of the product of the reaction is monobromocamphorsulphopiperidide, and

the production of this compound must have been the result of a partial oxidation of the piperidine present. It may be mentioned that an exactly similar change occurs when aa'-dibromocamphor and aa'-bromonitrocamphor are heated with piperidine, one atom of bromine in these substances being replaced by hydrogen.

When dibromocamphorsulphonic bromide is heated, decomposition occurs, sulphur dioxide being evolved and a new tribromocamphor formed; this melts at a temperature far below the melting point of $a\pi$ -dibromocamphor, and its properties at once recall those of ordinary aa'-dibromocamphor. Thus it is very stable towards strong nitric acid, but in presence of silver may be readily oxidised by the dilute acid; its alcoholic solution, when mixed with alcoholic silver nitrate, at once begins to deposit silver bromide; it is rapidly attacked by alcoholic potash, one bromine atom being lost and $a\pi$ -dibromocamphor produced; when, moreover, $a\pi$ -dibromocamphor is heated with bromine in a closed tube, the new tribromocamphor is the only product. Its relationship to $a\pi$ -dibromocamphor is therefore doubtless of the same nature as that of aa'-dibromocamphor to a-monobromocamphor. The substance is, therefore, $aa'\pi$ -tribromocamphor,

its structure being probably $CH_2Br \cdot C_7H_{11} < \stackrel{CBr_2}{CO}$.

The following scheme represents, in an abbreviated manner, the relationships which have been established between the various products:—



EXPERIMENTAL.

aa'-Dibromocamphoreulphonic acid, $C_{10}H_{18}Br_2O\cdot SO_8H$.

Purified ammonium dibromocamphorsulphonate (20 grams) is placed in a thick-walled glass tube, together with 50 c.c. of water and a small, thin-walled closed tube containing the requisite amount of bromine

(10 grams), the latter being broken after the outer tube has been hermetically sealed. The whole is then heated at 110-120° during 3-6 hours, when, as a rule, the colour of the bromine has disappeared; the liquid in the tube either sets, on cooling, to a mass of shining needles, or crystallises when the interior of the opened tube is rubbed with a glass rod. Experiments made in this way, however, are not uniformly successful, as in some cases the liquid becomes black, owing to partial or complete carbonisation; it is difficult to say what precisely determines this effect, as of two tubes having nearly the same dimensions, filled apparently in the same manner and heated side by side, one may behave quite satisfactorily, and the other contain a black liquid. It may be stated, however, that carbonisation may be entirely, or almost entirely, obviated by employing a much larger quantity of water, but in that case crystals are not deposited on cooling, and the subsequent isolation and purification of the product becomes a matter of much greater difficulty.

The crystals consist, for the most part, of dibromocamphorsulphonic acid, contaminated with its ammonium salt and ammonium bromide, and may be separated from the strongly fuming liquid by filtration, preferably through asbestos, washed with a little water, and dried at 100°. The mass is then powdered, transferred to a dry flask, and extracted as rapidly as possible with boiling ethylic acetate, which leaves the ammonium salts practically untouched; the filtered liquid, which quickly becomes dark coloured, should be rapidy evaporated to dryness, and the residual mass recrystallised from water to which animal charcoal has been added.

The acid prepared in this way was shown to be identical with that obtained during the oxidation of ammonium bromocamphorsulphonate with nitric acid, by a direct comparison of the two substances, and by the fact that when its aqueous solution was warmed with silver nitrate, silver bromide was formed, and on filtering from this and evaporating to dryness, the lactone, $C_{10}H_{12}Br_2SO_4$, melting at $188-189^\circ$ was obtained.

The acid crystallises with water, apparently in several different proportions, and some of this water is obstinately retained at temperatures considerably above 100°, and even after fusion, owing to the fact that lower hydrates of high melting point crystallise from the hot liquid. Thus, as obtained by very slow evaporation of the aqueous solution, the crystals melt, somewhat indefinitely, below 100°, the exact temperature depending on the rate of heating; when obtained under other conditions, by rapid crystallisation from hot water, or by allowing the foregoing crystals to effloresce, it melts at 128—133°, giving off water vapour, and solidifies at a slightly higher temperature; further heating causes it to melt at 156—159°,

which is the melting point of crystals from aqueous solution which have been dried for a short at 100° , or of those obtained from a solution in moist ethylic acetate. The substance melting at $156-159^{\circ}$, however, is not anhydrous, but seems to contain $1H_2O$, which is only slowly driven off at 100° , and is even retained for a considerable time at above 130° .

A second analysis of the substance melting at 156—159° was made in order to determine exactly what proportion of water it contained.

```
\begin{array}{lll} 0.3129 \ \text{gave} \ 0.3407 \ \text{CO}_2 \ \text{and} \ 0.1071 \ \text{H}_2\text{O}. & C=29.7 \ ; \ \mathbf{H}=3.8. \\ 0.2266 \ \ , & 0.2102 \ \text{AgBr}. & \text{Br}=39.5. \\ C_{10} H_{18} \text{Br}_2 \text{O} \cdot \text{SO}_3 H + H_2 \text{O requires} \ C=29.4 \ ; \ H=3.9 \ ; \ \text{Br}=39.2 \ \text{per cent.} \end{array}
```

The only satisfactory method of obtaining a nearly anhydrous substance was by dissolving the hydrated acid in hot, dry ethylic acetate and adding light petroleum until a distinct cloudiness, partly due to the separation of water, was observed; the whole was shaken and the clear hot liquid decanted, the crystals which separated on cooling being submitted to repeated treatment of this kind until a substance of constant melting point was obtained. In this way, the acid was obtained in small, glistening prisms, much less soluble in dry ethylic acetate than before; it melted and charred at 245—252°.

A small quantity was heated for some time at 100° and analysed.

```
0.2658 gave 0.2972 CO<sub>2</sub> and 0.0861 H<sub>2</sub>0. C=30.5; H=3.6.
0.2421 ,, 0.2334 AgBr. Br=41.2.
```

 $C_{10}H_{14}Br_2SO_4$ requires C = 30.8; H = 3.6; Br = 41.0 per cent.

Although, as was stated in the original paper, the acid loses a portion of its bromine when boiled with excess of alkali or even with metallic carbonates, it was found possible, when operating with larger quantities of material, to prepare many of the salts in a state of purity. A strong solution of the acid was heated on the water-bath, and nearly neutralised by gradually adding to it the solid carbonate of the metal, the liquid being then filtered and allowed to cool, when, as a rule, the salt separated in characteristic crystals, which could be purified by recrystallisation from hot water.

Ammonium aa'-dibromocamphorsulphonate, C₁₀H₁₄Br₂·SO₃·NH₄, crystallises from water in short, tufted, shining, apparently flattened needles. It is much more readily soluble in water than the ammonium salt of the monobromo-acid, which it resembles somewhat in appearance; it is also very readily soluble in alcohol, but is nearly insoluble in acetone or ether.

Its aqueous solution gives no precipitates with neutral salts of any of the metals of common occurrence; a solution of basic lead acetate, however, gives a very bulky, white precipitate which has no appearance

of crystalline structure under the microscope. If the solution of the ammonium salt is made alkaline with ammonia, warmed, and neutralised with nitric acid, silver nitrate produces an immediate precipitate of silver bromide; as the pure ammonium salt yields no precipitate, the readiness with which the bromine is eliminated from the acid is thus clearly demonstrated. Silver bromide is also gradually precipitated when the solution of the ammonium salt is boiled with silver nitrate.

The salt is anhydrous; an air-dried specimen gave the following results on analysis:

1.5184 lost only 0.0038 at 120°.

0.2531 gave 0.2320 AgBr. Br = 39.0.

 $C_{10}H_{13}Br_2O\cdot SO_8\cdot NH_4$ requires $Br = 39\cdot 3$ per cent.

It is optically active, as are all the derivatives of the axid described in this paper.

A solution of 1.5146 grams in 50 c.c. of water at 18°, examined in a 3-decimetre tube in polarised light, gave as a mean of 14 concordant measurements $a_D = +4^{\circ}41'$:

Hence
$$[a]_D = +51.5^\circ$$
.

The sodium salt is very readily soluble in water, alcohol, or acetone, and crystallises from the last in fine, colourless needles; the crystals obtained from water effloresce very quickly on exposure to the air.

The potassium salt, $C_{10}H_{13}Br_2O\cdot SO_3K + 4H_2O$, is very readily soluble in water and dissolves sparingly in alcohol; it crystallises in well-defined, flattened prisms, or in fine needles. A specimen crystallised from water and dried in the air was analysed.

0.3220 lost 0.0450 H_2O at 130° and gave 0.0539 K_2SO_4 . $H_2O = 14.0$; K = 7.5.

 $C_{10}H_{18}Br_2SO_4K + 4H_2O$ requires $H_2O = 14.4$; K = 7.8 per cent.

The calcium salt, $(C_{10}H_{18}Br_2O\cdot SO_8)_2Ca + 10H_2O$, is not very readily soluble in cold water. It crystallises in flattened prisms or needles having a satiny lustre. An air-dried specimen was analysed.

0.4738 lost 0.0890 H₂O at 130° and gave 0.0602 CaSO₄. H₂O = 18.7; Ca = 3.7.

 $(C_{10}H_{18}Br_2SO_4)_2Ca + 10H_2O$ requires $H_2O = 18.0$; Ca = 4.0 per cent.

The barium salt, $(C_{10}H_{18}Br_2O\cdot SO_8)_2Ba+15H_2O$, is somewhat sparingly soluble in cold water, and insoluble in alcohol or acetone; it crystallises from hot solutions in magnificent, long, shining needles which quickly effloresce on exposure, but retain their shape during the change.

0.4303 lost 0.0959 at 130° and gave 0.0833 BaSO₄. $H_2O = 22.3$; Ba = 11.4.

 $(C_{10}H_{13}Br_2SO_4)_2Ba + 15H_2O$ requires $H_2O = 22.8$; Ba = 11.5 per cent.

The zinc salt, $(C_{10}H_{13}Br_2O\cdot SO_3)_2Zn + 15H_2O$, which is readily soluble in cold water, crystallises in beautiful, white needles having a satiny lustre. An air-dried specimen gave the following results on analysis.

0.2703 lost 0.0653 at 150°. $H_2O = 24 \cdot 1$. 0.2247 gave 0.1484 AgBr. $Br = 28 \cdot 1$. $(C_{10}H_{18}Br_2SO_4)_2Zn + 15H_2O$ requires $H_2O = 24 \cdot 3$; $Br = 28 \cdot 7$ per cent.

The cadmium salt crystallises, according to the speed of separation, either in long, fine needles, or in large, thin, six-sided orthorhombic plates which quickly effloresce on exposure. It dissolves very readily in water.

The copper salt forms flat, light-blue needles, and dissolves very readily in water and in acctone.

The lead salt is sparingly soluble in cold, but dissolves readily in hot, water, and separates from hot water, which should be acidified with acetic acid, in large, globular masses, consisting of aggregates of very slender, white needles. A basic lead salt also exists, and is obtained as a bulky, white precipitate on adding basic lead acetate to a solution of ammonium dibromocamphorsulphonate; it is practically insoluble in water.

Dibromocamphorsulphonic chloride, C10H18Br2O·SO2Cl, is made from the crude ammonium salt or from the acid itself by triturating it with phosphorus pentachloride in the usual manner, and after pouring into water, is washed on a filter with a large quantity of water, and when dry crystallised from acetone. It dissolves somewhat sparingly in ether, chloroform, or acetic acid, more readily in ethylic acetate, benzene, or toluene, and still more readily in acetone, but is nearly insoluble in petroleum. It separates from ethylic acetate or acetone, when rapidly evaporated, in the form of small, hemihedral orthorhombic needles exactly resembling crystals of magnesium sulphate in appearance; on slow evaporation, however, it is deposited in magnificent, transparent, pyramidal crystals having the lustre of calcite. It melts and decomposes at 203-204°, slowly evolving sulphur dioxide, and darkens during the process. It dissolves readily in hot, strong nitric acid, but is scarcely affected by it, and after the solution has been boiled for 10 minutes and then cooled, it deposits the greater part unchanged. With water, it may be boiled for days without suffering any great alteration, although a small amount of hydrolysis appears to take place, for the liquid slowly becomes acid in

reaction; it is, however, rapidly hydrolysed and decomposed by hot alkali, with the loss of both chlorine and bromine.

A specimen crystallised from acetone and dried at 100° gave the following results on analysis.

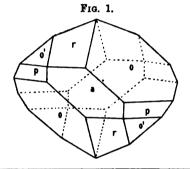
0.2542 gave 0.2701 CO₂ and 0.0748 H₂O. C = 29.0; H = 3.3. 0.2033 , 0.2595 AgCl + AgBr. Br + Cl = 48.0. $C_{10}H_{12}Br_{2}SO_{2}Cl$ requires C = 29.4; H = 3.2; Br + Cl = 47.8 per cent.

The crystals were measured and the following results obtained.

Crystalline system.—Orthorhombic. Sphenoidal hemihedrism.

$$a:b:c=0.8729:1:0.8550.$$

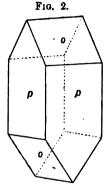
Forms present.— $\alpha = \{100\}$, $o = \kappa\{111\}$, $o' = \kappa\{1\overline{1}1\}$, $p = \{110\}$, $r = \{101\}$



Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$pp = 110 : \underline{110}$	22	82° 0′— 82°46′	82°14′	
$pp = 110 : \overline{1}10$	22	97 85 97 53	97 48	97°46′
op = 111:110	20	37 15 — 37 59	37 24	 -
$\dot{\omega} = 111 : \overline{11}1$	14	104 28 —105 23	104 57	104 52
$00 = 111 : \bar{1}11$	12	78 8 73 86	73 16	73 20
$oo' = 111 : 1\overline{1}1$	8	62 10 63 20	62 35	62 50
ap = 100:110	20	40 55 — 41 12	41 6	41 7
ao = 100:111	10	58 11 — 53 27	58 20	58 20
or = 111:101	6	81 7 — 81 49	81 81	81 25
	1			1

The crystals are transparent, colourless octahedra, prisms, or tetrahedra. When large crystals are obtained by slow evaporation, their hemihedrism is usually scarcely evident, owing to the very irregular development of the crystals as a whole. When small crystals are produced by more rapid evaporation, the hemihedrism is frequently well marked; minute crystals obtained by evaporating a drop of the acetone solution on a watch glass or microscope slide are unmistakably

hemihedral as a rule, being small prisms truncated at each end by a pair of faces of the form $o = \kappa\{111\}$, the line of intersection of the pair at one end being therefore at right angles to that of the pair at the opposite end. The general form of these small prisms is shown in Fig. 2.



In general, the forms most frequently developed are $p = \{110\}$ and $o = \kappa\{111\}$, and very frequently also $o' = \kappa\{1\overline{1}1\}$. The forms $a = \{100\}$ and $r = \{101\}$ occur as a rule only on the larger crystals, and frequently are only partially represented. All the faces are brilliant and give good images. There appears to be no definite cleavage.

Dibromocamphorsulphonic Bromide, C₁₀H₁₈Br₂O·SO₂Br.—This substance has already been partly described and also measured (Trans., 1897, 71, 24), and may be readily obtained from the ammonium salt, or from the acid itself, by interaction with phosphorus pentabromide or a mixture of phosphorus trichloride and bromine. Its identity with the substance previously described as hydroxydibromocamphorsulphonic bromide was proved by a comparison of the chemical and crystallographic properties. Both melted at 193—194°, evolving sulphur dioxide. Some of the crystals prepared by the new method were measured, and gave the following results, the numbers in the last column being those observed, or calculated from those observed, in the original crystals:

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$pp = 110: 1\overline{10}$ $op = 111: 110$ $oo = 111: \overline{110}$ $oo' = 111: \overline{11}$ $ar = 100: 101$ $ap = 100: 110$	6 6 6 4 4	81°27′— 81°42′ 87 42 — 88 12 103 55 —104 30 61 8 — 62 30 45 35 — 46 3 40 32 — 41 3	81°31′ 37 41 104 15 62 18 45 41 40 41	81°35′ 37 58 104 4 61 59 45 52 40 48

The crystals closely resemble those of the sulphonic chloride, and it will be noticed that in the present case the pinacoid $a = \{100\}$ and the dome $r = \{101\}$ are represented, although they were not observed in the crystals first examined. It was noticed that the crystals in a high state of purity, especially when large, did not evince so markedly the hemihedrism observed when they were smaller and perhaps less pure. It is always possible, however, to demonstrate their hemihedral nature by allowing a drop of a solution of one of them to evaporate, when the small crystals obtained exactly resemble those of the sulphonic chloride depicted in Fig. 2 obtained by a similar method.

Dibromocamphorsulphonamide, C₁₀H₁₈Br₂O·SO₂NH₂, is obtained by the action of aqueous ammonia on the powdered sulphonic chloride or bromide in the cold. It is very sparingly soluble in alcohol, sparingly also in acetic acid or acetone, and almost insoluble in ether, benzene, or light petroleum. It is best crystallised from acetone, from which it separates in hard, transparent prisms or needles, and melts and chars at about 238°.

A specimen dried at 100° was analysed.

0.2223 gave 0.2513 CO₂ and 0.0814 H₂O. C = 30.7; H = 4.0.

0.1721 , 0.1677 AgBr. Br = 41.4.

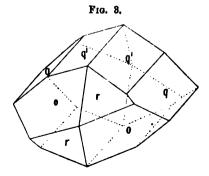
 $C_{10}H_{15}Br_{2}SO_{8}N$ requires C = 30.9; H = 3.9; Br = 41.2 per cent.

A few crystals were obtained of sufficient size for measurement, and gave the following numbers.

Crystalline system.—Orthorhombic. Sphenoidal hemihedrism.

Axial ratio a:b:c=0.4954:1:0.9073.

Forms observed:— $o = \kappa\{111\}, r = \{101\}, q = \{011\}, q' = \{012\}.$



Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$qq = 011:0\overline{1}1$ $oo = 1\overline{1}1:11\overline{1}1$ $oq = 1\overline{1}1:0\overline{1}1$ $qq' = 011:012$ $q'q' = 012:01\overline{2}$ $or = 1\overline{1}1:10\overline{1}$ $rr = 101:10\overline{1}$ $or = 1\overline{1}1:10\overline{1}$ $qr = 0\overline{1}1:10\overline{1}$ $qr = 0\overline{1}1:10\overline{1}$ $qr' = 1\overline{1}1:0\overline{1}2$	18 20 14 16 20 5 4 4 8	83°31′—84°51′ 72 28 —78 13 52 59 —53 55 16 28 —18 25 48 25 —49 43 23 10 —23 59 56 41 —58 1 59 1 —60 52 63 53 —64 50 54 54 —55 49	84°26′ 72 48 53 84 17 22 49 20 23 45 57 81 59 58 64 82 55 17	53°36′ 17 49 48 48 23 30 57 16 60 16 64 7 55 36

The crystals, as a rule, are long needles or prisms, but are occasionally quite short, and then present very much the appearance shown in the diagram. All the crystals examined exhibited the hemihedrism very distinctly. They are transparent and glass-like in appearance and fairly hard. The faces in the prism zone were usually very badly developed, affording multiple images, owing to a curious step-like structure, but in the case of the forms $o = \{1\overline{1}1\}$ and $r = \{101\}$ the images were single and very bright.

Dibromocamphorsulphonamide is slightly soluble in ammonia and dilute alkalis, and is reprecipitated unchanged, on addition of acids, little or no halogen seeming to be eliminated during the process. It dissolves in strong potash, however, losing much bromine, and the liquid becomes dark coloured, but does not evolve any appreciable quantity of ammonia. If, after some hours boiling, the liquid is diluted and acidified, no precipitate is produced, and if then neutralised with sodium carbonate and treated with a 1 per cent, solution of potassium permanganate, the colour of the latter is at once discharged. As it seemed probable that some unsaturated compound had been produced. attempts were made to extract it from the acidified solution; ether. amylic alcohol, chloroform, &c., failed to dissolve any appreciable quantity of organic matter, and it was therefore saturated with calcium chloride and extracted with acetone. In this way, a small quantity of a sparingly soluble syrupy substance was obtained, which did not afterwards dissolve in water, and was apparently saturated. Further attempts to obtain the unsaturated substance proved unavailing, and it seems probable, therefore, that it was a sulphonic acid, which, owing to its high dissociation constant, it would be practically impossible to extract from aqueous solution.

Action of Piperidine on Dibromocamphoreulphonic Chloride.

When dibromocamphorsulphonic chloride is shaken with an ethereal solution of piperidine, it dissolves slightly, and the residue becomes pasty; in the course of a few hours, however, it again becomes solid, and presents the appearance of a granular, greyish mass. In one experiment, the ether was allowed to evaporate at the ordinary temperature, and the mass was then ground up with dilute hydrochloric acid, filtered, washed with plenty of water, and dried. The residue was repeatedly crystallised from benzene, chloroform, or other solvents, and the various fractions gradually became viscid, probably due to a gradual combination with water, either contained in the solvents or attracted from the air, for they were finally found to dissolve in water and to consist of a mixture of piperidine salts of sulphonic acids. A slight residue insoluble in water was also obtained, but examination showed it to be a mixture.

The following method was finally adopted as affording better results. The powdered sulphonic chloride was carefully sifted into about 10 times its weight of piperidine, the whole being then ground up in a mortar to free it from lumps, and finally transferred to a flask and heated on the water-bath for 6 hours. The turbid liquid was poured into dilute hydrochloric acid, and after being left for several days, the insoluble portion was separated by filtration, and formed a greyishwhite, pulverulent mass, which was dried at 100° and crystallised. After repeated fractionation from dilute alcohol and then from ethylic acetate, two kinds of crystals were recognised; one set consisted of colourless, slender needles or prisms, and the other of bright yellow The details of the tedious separation need not be given, but it may be said that the most speedy method of effecting it is to obtain the mixture in which the two substances may be distinguished, and to separate them mechanically as far as possible, for, since their solubilities in all solvents tried are nearly identical, the ordinary method is unusually lengthy. The yellow substance may then be purified by recrystallisation from benzene, and the white one from ethylic acetate.

A specimen of the colourless substance, crystallised from ethylic acetate and dried at 100°, gave the following results on analysis:

```
0.2452 gave 0.3496 CO_2 and 0.1108 H_2O. C = 38.9; H = 5.0. 0.1100 , 0.0915 AgBr. Br = 35.4.
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 $C_{15}H_{23}Br_2SO_3N$ requires C = 39.3; H = 5.0; Br = 35.0 per cent.

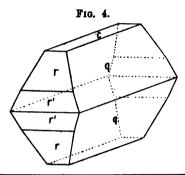
The substance was therefore dibromocamphorsulphopiperidide, $C_{10}H_{13}Br_2O \cdot SO_2 \cdot NC_5H_{10}$. It dissolves very readily in benzene, acetone,

chloroform, or acetic acid, less readily in alcohol or ethylic acetate, and very sparingly in petroleum; it appears to be insoluble in water or alkalis. It crystallises from hot, dilute alcohol in colourless, glistening needles, and from ethylic acetate, on spontaneous evaporation, in nearly colourless, transparent plates or prisms and melts at 157—158°. The crystals were measured with the following results:—

Crystalline system :- Orthorhombic, holohedral.

Axial ratio, a:b:c=1.9896:1:2.2728.

Forms observed:— $r = \{101\}, r' = \{201\}, q = \{011\}, c = \{001\}.$



Angle.	Number of measurements.	Limits.	Mean.	Calculated
cq =001:011 cr =001:101 cr'=001:201 rr'=101:201 qr =011:101 qr'=011:201	20 15 14 14 4 8	65°17′—67°17′ 48 3 —49 7 65 85 —67 1 16 85 —17 26 74 0 —74 48 80 8 —80 54	66°15′ 48 48 66 29 17 21 74 15 80 20	66°22′ 17 34 74 87 80 42

The crystals were obtained in two distinct forms. In the smaller crystals, the habit was plate-like, shortening in the direction of the c axis having taken place, and in this case the forms r and r' were equally well developed as a rule; the larger crystals assumed a more prism-like habit, being extended in the direction of the c axis. In the latter instance, the form r was developed to the exclusion of r' as a rule, but individuals were obtained in which r' was partially represented. The crystals were transparent and nearly colourless when small, but when large exhibited a faint brownish tint. The faces, as a rule, gave poor images, more especially those of the forms r and r', although these were usually the smallest on the crystal.

It was not found possible to obtain dibromocamphorsulphopiperidide in theoretical quantity from either the chloride or the bromide by any method tried. On treatment with alcoholic potash, bromine is eliminated fairly readily, and the product appears to contain the yellow substance above mentioned; it slowly loses bromine, also, when it is heated with piperidine, especially at temperatures above 100°, but the product is not easy to purify; doubtless the same substance is obtained as when alcoholic potash is used.

The yellow crystals gave the following results on analysis:

0.1038 gave 0.1802 CO₂ and 0.0608 H₂O. C = 47.3; H = 6.5.

0.1215 , 0.0608 AgBr. Br = 21.3.

 $C_{15}H_{14}BrSO_8N$ requires C = 47.6; H = 6.4; Br = 21.2 per cent.

The substance therefore had the composition of a monobromo-camphorulphopiperidide, $C_{10}H_{14}BrO\cdot SO_2\cdot NC_5H_{10}$.

It crystallised from benzene in curious lamellated plates, the sides of which were deeply furrowed by pits; its colour when obtained in the above manner, was a bright yellow, although in all probability this was merely due to impurity, to which it obstinately adhered. It melted at 152°, and its solubility in most liquids closely resembled that of the dibromocamphorsulphopiperidide.

In order to determine its true nature, it was made by heating powdered monobromocamphorsulphonic chloride on the water-bath with two molecular proportions of piperidine for some hours; a substance was thus obtained in nearly colourless crystals, which, after two crystallisations, melted at 139—142°, and even after repeated recrystallisations, failed to attain the melting point of the yellow crystals by 3° or 4°. That the two substances were nevertheless identical was shown by a comparison of their crystalline form, solubility, and general properties; when mixed and heated in a capillary tube, the melting point of the mixture was intermediate between those of the separate constituents. The difference in melting point was evidently due to some impurity in the second specimen difficult to remove. Crystals good enough for measurement were not obtained.

Action of Alkalis on Dibromocamphorsulphonic Acid.

As already mentioned, dibromocamphorsulphonic acid readily loses bromine when treated with alkalis, or even with alkali carbonates. The earlier attempts to isolate the products proved fruitless, however, no doubt in consequence of the difficulty, always experienced with fatty sulphonic acids, that the presence of impurities retards or entirely prevents their assuming a crystalline form. The following experiment was therefore made, in the hope of avoiding this difficulty.

Crystallised dibromocamphorsulphonic chloride (10 grams) was added to a very large excess of caustic potash dissolved in about

three times its weight of water, and heated nearly to boiling on a sand-bath for an hour; after cooling, the liquid was neutralised, evaporated to dryness, and the solid residue powdered and triturated in a mortar with about 25 grams of phosphorus pentachloride, the mass being afterwards mixed with ice, when black, sticky clots remained undissolved. These were extracted with chloroform, in which they dissolved readily, and the extract, after being washed repeatedly with a dilute solution of sodium carbonate, was dried and evaporated; the transparent, gum-like residue for a long time refused to crystallise, even after fractionation from light petroleum, but it was found that, after boiling with anhydrous formic acid, a semicrystalline powder was deposited in considerable amount. collected on a filter, drained on a porous tile, and crystallised from hot petroleum, brilliant crystals being deposited, which melted at 135°. They gave the following result on analysis.

0.2561 gave 0.3470
$$CO_2$$
 and 0.1002 H_2O . $C = 36.4$; $H = 4.3$. $C_{10}H_{14}BrSO_3Cl$ requires $C = 36.9$; $H = 4.3$ per cent.

As the substance seemed to be bromocamphorsulphonic chloride, $C_{10}H_{14}BrO\cdot SO_2Cl$, it was compared with a specimen prepared in the ordinary manner, when the two agreed in all respects, as did the bromides and the dibromocamphors prepared from them.

When dibromocamphorsulphonic bromide is heated at its melting point, sulphur dioxide is evolved (*loc. cit.*), but owing to further decomposition, as evidenced by much darkening, a definite product could not be isolated.

When perfectly pure dibromocamphorsulphonic bromide is quickly heated, a slight darkening only is noticed at first, and if the process is interrupted before the evolution of gas is at an end, it is not difficult to isolate the new substance from the product. Powdered dibromocamphorsulphonic bromide, in quantities of not more than a gram, is strewn over the bottom of a thin beaker heated at 210° by means of a fusible metal bath. The substance melts and froths up, sulphur dioxide, and finally a little hydrogen bromide, being evolved; at this point (after about 1 minute) the action is stopped, and the beaker allowed to cool. The products of several such experiments, which contain unaltered sulphonic bromide and carbonaceous matter, are mixed together and boiled for about 5 minutes with strong nitric

acid of sp. gr. 1.42, when the colour of the solution gradually disappears, the sulphonic bromide and other impurities being destroyed or rendered soluble in water; the cooled liquid is then diluted and filtered, the insoluble residue being finally purified by crystallisation from dilute alcohol.

A specimen prepared in this way was dried over sulphuric acid in a vacuum and analysed:

```
0.2414 gave 0.2755 CO<sub>2</sub> and 0.0744 H<sub>2</sub>O. C=31.1; H=3.4.
0.1296 ,, 0.1863 AgBr. Br=61.2.
C_{10}H_{10}Br_{0}O requires C=30.8; H=3.3; Br=61.7 per cent.
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aa'π-Tribromocamphor is readily soluble in ethylic or methylic alcohol, benzene, ether, acetone, or acetic acid, and is somewhat readily soluble in petroleum; it crystallises from these solvents in long, colourless needles, and melts at 69-70°. It is very stable towards oxidising agents, and may be boiled for a long time with strong nitric acid without appreciable alteration. It readily loses bromine, however, when its alcoholic solution is warmed with silver nitrate. but owing to the small quantity of material at the author's disposal, it was not found possible to isolate the product; bromine is also eliminated when the substance is boiled with alcoholic or even with aqueous caustic potash. In order to isolate the product of the latter action, strong alkali was used; the substance melted to a clear liquid as the temperature was raised, and towards the end of the reaction became a mass of crystals. These were separated by filtration, washed with water, and crystallised from acetic acid, from which the substance was deposited in beautiful, transparent needles, which melted at 152° and had all the properties of aπ-dibromocamphor.

This reaction, as well as its mode of formation, having indicated that the above tribromocamphor stood in the same relationship to $a\pi$ -dibromocamphor as aa'-dibromocamphor does to a-monobromocamphor, it became necessary to ascertain whether it could not be obtained from $a\pi$ -dibromocamphor by direct bromination. It was found that no action occurred between bromine and $a\pi$ -dibromocamphor at the temperature of the water-bath; they were therefore mixed in molecular proportion and heated in a closed tube with a little acetic acid at 120° during 4 hours. On fractionally crystallising the product from dilute alcohol, a large quantity of unaltered dibromocamphor was obtained, together with a more soluble substance, which crystallised in silky needles melting at 69—70° and having all the properties of the tribromocamphor made by the former process.

Most of the expense incurred in the investigation described in this paper has been defrayed by a grant from the Research Fund of the Chemical Society, for which the author desires to acknowledge his indebtedness.

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LVI.—Crystalline Glycollic Aldehyde.

By HENRY J. HORSTMAN FENTON, M.A., and HENRY JACKSON, B.A., B.Sc.

GLYCOLLIC aldehyde, or diose, is of especial interest, as being the first true representative of the "sugars," these being defined as aldehydealcohols, or ketone-alcohols. Unsuccessful attempts to prepare this substance were made in the first instance by Abeljanz from dichlorether, and by Pinner from glycol-acetal, but Fischer and Landsteiner afterwards succeeded in obtaining it in solution by acting on a solution of bromaldehyde with baryta at 0° (Ber., 1892, 25, 2549); Marckwald and Ellinger also obtained a solution of the substance by the action of dilute hydrochloric or sulphuric acid on glycol-acetal (Ber., 1892, 25, 2984). The present authors have also recently obtained it in solution by the oxidation of glycol in presence of iron (this vol., 2).

During a study of the properties of dihydroxymaleic acid, it was found by one of the authors (Trans., 1895, 67, 774) that this acid, when heated with water, splits up almost quantitatively into glycollic aldehyde and carbon dioxide, $C_4H_4O_6 = C_2H_4O_2 + 2CO_2$. The decomposition begins slowly, even at the ordinary temperature, and becomes very rapid at 50-60°. A small quantity of acid (probably glyoxylic acid) is produced at the same time, but this can be removed by neutralisation with calcium carbonate, evaporation in a vacuum desiccator, and extraction with absolute alcohol. The alcoholic solution thus obtained, when similarly evaporated, leaves a colourless, sweettasting syrup, which refuses to crystallise. Traces of alcohol are obstinately retained in this product, however; even after 6 days exposure in a vacuum desiccator, the numbers obtained on analysis were C = 40.81, H = 7.01, theory requiring C = 40.00, H = 6.66 per cent. It appeared very desirable to isolate the substance in a pure state, and many attempts were consequently made with this object.

If the transparent, syrupy product be repeatedly stirred with small quantities of anhydrous ether, it soon becomes opaque and viscid, and subsequent stirring with light petroleum (b. p. 40-70°), produces

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these effects in a more marked degree. The substance so treated, when kept for some time in a vacuum desiccator, becomes a stiff, wax-like solid, but here, again, traces of the solvent are obstinately retained; after exposure for about four weeks in a vacuum desiccator, with occasional stirring, a specimen treated in this manner gave, on analysis, C=40.53, H=6.95 per cent.

Since it appeared impossible absolutely to remove the last traces of solvent at the ordinary temperature, similar experiments were made at 40°. Heated at this temperature in a vacuum, the weight became nearly constant after about 24 hours; but an almost insignificant and nearly constant loss was still perceptible after continued heating, due, doubtless, to the volatility of the aldehyde itself. The product obtained in this way gave, on analysis, numbers agreeing well with those required by theory.

0.1416 gave 0.2079 CO₂ and 0.0862 H₂O. C = 40.04; H = 6.76.

This treatment has therefore had the desired effect of removing the solvent, but it is, of course, possible that polymerisation may have occurred. In order to investigate this question, the molecular weight was determined by the freezing point method with water as solvent.

	Wt. of solvent.	Wt. of substance.	Depression.	Mol. wt.
I.	19.94	0.3810	Õ∙ 2 95	121.7
II.		1.0262	0.732	$132 \cdot 1$

The values obtain correspond therefore with those required for the double formula, $C_4H_8O_4$ (=120), and consequently it appeared to be highly probable that the product was tetrose, especially as Fischer and Landsteiner had obtained an aqueous solution containing this substance by treating the glycollic aldehyde solution with weak caustic soda at 0° . In the present case, however, it was found that, on heating the solution with phenylhydrazine acetate at 40° for some hours, an osazone was obtained which, when recrystallised from hot absolute alcohol, melted at $168-169^\circ$, and resembled in every respect the osazone of glyoxal, $N_2HPh:CH:CH:N_2HPh$.

The most probable inference, therefore, appeared to be that the aldehyde had undergone partial condensation, and that the product examined was a mixture of unaltered glycollic aldehyde with a hexose. It will be presently shown, however, that these results may probably be explained in a different manner.

It was further shown (Trans., 1895, 67, 780; 1897, 71, 375) that the syrupy glycollic aldehyde, obtained as above described, if heated in a vacuum at about 100° , polymerises to a large extent, giving a hexose, which, when purified from unaltered glycollic aldehyde by means of hot alcohol, yields a normal hexosazone, $C_{18}H_{22}N_4O_4$. During this process of heating the aldehyde, a small quantity of

crystalline substance was frequently observed in the exit-tube of the apparatus employed, but its production seemed to be very uncertain, and the quantity obtained was too small for proper examination, Making closer observations, however, the authors have now found that this crystalline substance is invariably produced, but that it appears first as a syrupy liquid which often takes a very considerable time to crystallise. The latter circumstance accounts for the fact that it was often overlooked.

For the preparation of this crystalline product, in the first experiments, the syrupy glycollic aldehyde, prepared as above described and purified by calcium carbonate and alcohol, was employed; but it is now found that this purification is unnecessary for the purpose, and consequently that the process may be considerably accelerated and simplified.

The following is the outline of the method adopted: crystallised dihydroxymaleic acid is covered with a small quantity (about $2\frac{1}{2}$ times its weight) of water, the mixture heated at $50-60^{\circ}$ in the manner previously described (Trans., 1895, 67, 778), and after the action has ceased, the solution is distilled to a small bulk under greatly diminished pressure at a temperature not exceeding 40° . When the greater part of the water has come over, the temperature is gradually raised; the distillation proceeds now very slowly, and the volatile product becomes more viscid. Near 100° , it is quite syrupy, and these drops of liquid, when left for some hours, begin to crystallise, and after stirring soon set to a crystalline mass. The earlier portions of the distillate, collected after the temperature is raised above 40° , when concentrated in a vacuum desiccator at the ordinary temperature, yield a similar crystallisable syrup, so that if preferred the whole may be collected together and concentrated in this manner.

The crystals thus obtained are colourless, transparent, oblique plates which melt at 95—97°. When quickly heated in a vacuous tube to about 100—130°, they vaporise almost entirely, giving a liquid sublimate which, when stirred and left, sets to a mass of crystals. They have a sweet taste, and are fairly easily soluble in cold water or hot alcohol, but only very sparingly in ether; in boiling acetone, they dissolve with difficulty, and recrystallise as the solution cools, the crystals being identical with those originally obtained. For analysis, the original crystals were washed with anhydrous ether, well pressed, and kept in a desiccator.

I. 0.1251 gave 0.1828 CO₂ and 0.0751 H₂O. C = 39.85; H = 6.67. II. 0.1848 ,, 0.2710 CO₂ ,, 0.1084 H₂O. C = 39.97; H = 6.64. C₂H₄O₂ requires C = 40.00; H = 6.66 per cent.

The substance is optically inactive, as was of course to be expected.

Osazons.—A dilute aqueous solution of the substance, when mixed with phenylhydrazine acetate, gives, on standing, a considerable amount of orange-yellow, crystalline precipitate at the ordinary temperature, and the quantity is increased by heating at 40°, the yield after a few hours at this temperature being considerably more than twice the weight of the aldehyde taken. After recrystallisation from hot absolute alcohol, it is obtained in the characteristic rosettes of straw-coloured plates, melting sharply at 169°, and identical in every respect with that previously prepared in the experiments before mentioned (Trans., 1895, 67, 774, and this vol., 2). Analysis of this product, dried at 100°, gave the following result.

0.1135 gave 0.2928 CO₂ and 0.0603 H_2O . C = 70.35; H = 5.90. $C_{14}H_{14}N_4$ requires C = 70.58; H = 5.88 per cent.

Molecular weight.—This was determined as before by the freezing point method, using water as solvent.

Wt. of solvent. Wt. of substance. Depression. Mol. wt. I. 12.05 0.1326 0.184 112.4

This result, is, therefore, much too high for the single molecule, and approaches that required for the double value, $C_4H_8O_4=120$.

Crystalline glyceraldehyde has recently been obtained by Wohl (Ber., 1898, 31, 2394), and it was shown by him that the molecular weight of the substance in a freshly prepared solution approximates to the value required for the double formula $C_6H_{12}O_6$, but after the solution has remained at the ordinary temperature for 2 days the number corresponds with that for the single formula $C_8H_6O_3=90$, and it is suggested that the substance in the crystalline state is bimolecular, and, in solution, gradually changes to the monomolecular condition.

Bearing in mind these facts, it appeared probable that the crystalline aldehyde at present under consideration might exhibit a similar behaviour, the solution above mentioned was therefore left for about 24 hours and the freezing point again determined. The depression was now 0.322 in place of 0.184, the corresponding molecular weight being 64.2. Repeating the experiment on the following day, the depression observed was 0.336, which, corresponds with the value 61.5.

A second experiment gave practically the same results, as follows:

Wt. of solvent. Wt. of substance. Depression. Mol. wt. II. 15.71 0.1770 0.226 93.7

Repeating the experiment with the same solution on the following day, the depression was 0.346, corresponding with the molecular weight 61.2, and on the third day an exactly similar reading was obtained.

The calculated molecular weight of glycollic aldehyde being 60, it is evident that the substance behaves in this respect exactly in the same manner as crystalline glyceraldehyde.

Cupric Oxide Reducing Power.—Experiments show that 1 mol. of pure glycollic aldehyde reduces 2 atoms of copper from the cupric to the cuprous state, as will be seen by the following numbers.

0.2610 gram substance was dissolved in water, made up to 50 c.c., and the solution run into standard Fehling's solution. The reduction takes place rapidly in the cold, and is completed by heating on a water-bath.

25 c.c. of Fehling's solution containing 0.00876 Cu per c.c. required (1) 19.2 c.c. and (2) 19.9 c.c. of the above aldehyde solution; 60 parts by weight of the aldehyde therefore reduced 128 parts by weight of copper.

Experiments with Yeast.—These were conducted exactly in the manner described in a previous communication on a synthetical hexose, (Trans., 1897, 71, 376), the solution to be examined being carefully compared with a blank test and with a corresponding solution of grape-sugar. No indications of fermentation could be detected even after 2 days.

Having at command this direct and simple method for preparing glycollic aldehyde in a pure state, the authors intend to make a further study of its relations and properties. The condensation products are at present under investigation; in addition to the hexose previously described (loc. cit.), which was obtained by heating the aldehyde at 100°, other products are obtained when a higher temperature is employed, and some of these promise to be of great interest.

The isolation of glycollic aldehyde in the crystalline state, together with Wohl's recent isolation of glyceraldehyde, nearly complete the list of crystalline representatives of each member of the 'sugar' family. Tetrose has yet to be isolated; the authors are making experiments in this direction by the oxidation of erythritol in presence of iron (this vol., 8), and these experiments, as far as they have gone, are very encouraging.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for funds which have enabled them to carry out this investigation.

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LVII.—Diortho-substituted Benzoic Acids. Part IV. Formation of Salts from Diortho-substituted Benzoic Acids and different Organic Bases.

By LORENZO L. LLOYD and JOHN J. SUDBOROUGH.

It is well known that diortho-substituted benzoic acids and their derivatives behave in many respects quite differently from those benzoic acids in which the hydrogen atoms in the ortho-positions relatively to carboxylic groups have not been replaced. Among the more characteristic of these differences may be enumerated the following:

Etherification of Acids.—Meyer and Sudborough (Ber., 1894, 27, 510, 1580, 3146), Lepsius (ibid., 1635), Meyer (Ber., 1895, 28, 182, 1254, 2773, 3197; 1896, 29, 830, 1397), van Loon and Meyer (Ber., 1896, 29, 839) have shown that diortho-substituted benzoic acids do not yield etheric salts when their methyl alcoholic solutions are saturated with hydrogen chloride and allowed to remain at 0° during 12 hours; similar results have been obtained by boiling the acids with a 3 per cent, solution of hydrogen chloride for 3 hours. groups, CH, OH, COOH, F, Cl, Br, I, NO, have been shown to prevent the formation of etheric salts under these conditions. different results have been obtained by passing hydrogen chloride through a boiling alcoholic solution of the acid for several hours, for when the substituting groups are small (CH₂, OH, and F), minute quantities of etheric salt may be obtained, but when they are larger (NO₂, Cl, Br, I, &c.), no trace of it can be detected. In this way, the stereochemical influence of the ortho-substituting groups on the retardation or prevention of etherification has been shown to depend, not on the chemical nature of the group, but on its weight or size (compare Sudborough and Lloyd, this vol., 481). Somewhat similar results have been obtained by Goldschmidt (Ber., 1895, 28, 3224), and Kellas (Zeit. phys. Chem., 1897, 24, 221) for monosubstituted benzoic acids, but in neither case has any clear relationship between the retarding actions of different groups and their radicle weights or volumes been shown.

Hydrolysis of Etheric Salts.—The reseaches of V. Meyer on the etheric salts of diortho-substituted benzoic acids, and of Kellas on those of monortho-substituted acids (Zeit. phys. Chem., 1897, 24, 243) indicate that these etheric salts are more difficult to hydrolyse than those of substituted benzoic acids in which the ortho-positions are free. It does not follow, however, that the ortho-substituted acids when, arranged according to the ease with which they are

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etherified, follow the same order as when arranged according to the readiness with which their etheric salts are hydrolysed (Kellas).

Hydrolysis of Acid Chlorides, Amides, and Nitriles.—The effects of the introduction of substituents into the ortho-positions in benzoic chlorides and amides, and also to a certain extent in benzonitriles, have been investigated by Sudborough (Trans., 1894, 65, 1030; 1895, 67, 587, 601), V. Meyer (Ber., 1894, 27, 3153), Sudborough, Jackson, and Lloyd (Trans., 1897, 71, 229), and Remsen (Chem. News, 1897, 75, 200). It has been shown that diortho-substituted benzoic chlorides, when boiled with an 8 per cent. aqueous solution of sodium hydroxide, are much more difficult to hydrolyse than isomeric benzoic chlorides, and similar results have been obtained by heating the corresponding amides with 75 per cent. sulphuric acid.

As already pointed out (Trans., 1897, 71, 234), Wegscheider (Monats., 1895, 16, 65) has sought to account for the abnormal behaviour of diortho-substituted benzoic acids on etherification by reintroducing Henry's theory. According to Henry, the formation of an etheric salt by the hydrogen chloride method is preceded by the direct addition of a molecule of alcohol to a molecule of the acid,

$$R \cdot C \triangleleft_{OH}^{O} \quad \rightarrow \quad R \cdot C \triangleleft_{OH}^{OEt} \quad \rightarrow \quad R \cdot C \triangleleft_{O}^{OEt}.$$

If this is so, then a similar additive reaction may take place during the hydrolysis of acid chlorides, amides, and etheric salts, for example:

$$R \cdot C \triangleleft_{\operatorname{Cl}}^{\operatorname{O}} \quad \to \quad R \cdot C \triangleleft_{\operatorname{Cl}}^{\operatorname{OH}} \quad \stackrel{\cdot}{\to} \quad R \cdot C \triangleleft_{\operatorname{O}}^{\operatorname{OH}}.$$

Wegscheider's conclusion has received considerable support from a recent investigation by Pechmann (Ber., 1898, 31, 501). Claisen has shown that etheric salts, as a rule, can combine with sodium ethoxide,

yielding additive compounds of the type R·COEt, but, according

to Pechmann, etheric salts of diortho-substituted benzoic acids are incapable of forming such compounds.

Analogy would suggest that diortho-substituted aldehydes or ketones may possess somewhat similar properties (compare Trans., 1897, 71, 234; Wegscheider, loc. cit.). Investigations on the formation of oximes and hydrazones have been made by Meyer (Ber., 1896, 29, 835), but the results are not quite so general as those obtained with the acids; moreover, it is not certain that the reaction between an aldehyde or a ketone and hydroxylamine or phenylhydrazine is an additive reaction.

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The researches of Emil Fischer and Giebe (Ber., 1897, 30, 3053; 1898, 31, 545) also show that the formation of acetals from benzaldehydes and alcohols under the influence of hydrogen chloride is not retarded, when substitution takes place in both ortho-positions in the aldehyde, neither are the diortho-substituted acetals more difficult to hydrolyse than those which are not diortho-substituted; it is thus evident that the formation and hydrolysis of acetals are reactions which are not influenced, to any appreciable extent, by stereochemical influences.

The hydrolysis of an acetal, R·C OEt, certainly cannot be an additive

reaction in the same sense as the hydrolysis of an etheric salt as described above, and whether the conversion of an aldehyde,

$$R \cdot C < \stackrel{O}{\leftarrow}_{H}^{O}$$
, into an acetal, $R \cdot C < \stackrel{OEt}{\leftarrow}_{H}^{OEt}$, is to be regarded as a true

additive reaction is somewhat questionable.

Very little work appears to have been done on the effect of stereochemical influences on reactions of aldehydes and ketones which are undoubtedly additive, for example, combination with sodium hydrogen sulphite, with hydrogen cyanide, &c.; but arguing from analogy, it would be safe to predict that diortho-substituted benzaldehydes will be found to be incapable of forming such derivatives. Up to the present, we have had no opportunities of confirming this conclusion.

The researches which so far have been carried out lead to the conclusion that diortho-substituted compounds of the type



where Y may be OH, Cl, NH₂, and probably H and CH₃ are either incapable of forming additive compounds by the addition of any molecule to the carbonyl group, or they yield them with the greatest difficulty.

No investigations have been made in order to determine whether an additive reaction of a different kind, for example, the direct addition of an amine to a substituted benzoic acid, is dependent on stereochemical influences. Experiments have been undertaken to determine whether the stereochemistry of the basic and also of the acid molecules plays any important part in the reaction, as we wished to ascertain whether a tertiary amine, such as tribenzylamine, containing large alkylic groups, would combine with a diortho-substituted benzoic acid as easily as an amine of low molecular weight. Further, we thought it worth while to determine whether any great difference in their capacity to combine with the same acid would be exhibited between isomeric bases such

as pseudocumidine and mesidine, or between 2:4-dibrom- and 2:6-dibrom-aniline. That all additive reactions are not largely dependent on stereochemical influences has been shown in the case of substituted iodobenzenes by McCrae (Trans., 1898, 73, 691), who has proved that the introduction of substituents into the two ortho-positions relatively to the iodine atom does not prevent the formation of an iodochloride by the direct addition of two atoms of chlorine. It appeared interesting to determine, therefore, whether the ortho-groups in a diortho-substituted aniline would hinder or prevent the conversion of tervalent into quinquevalent nitrogen.

The acids we selected were 2:4:6-trinitrobenzoic acid, 2:4:6-tribromobenzoic acid, and 2:4:6-tribromo-3-amidobenzoic acid, both because the groups in the ortho-positions in these acids are among those which have the greatest retarding action on etherification, and also because the acids are among the most readily obtainable diorthosubstituted benzoic acids. In order to compare their behaviour with benzoic acids in which this condition was absent, we investigated the combination of amines with benzoic acid and with metanitrobenzoic acid. The bases employed were trimethylamine, tripropylamine, tribenzylamine, aniline, metabromaniline, metanitraniline, 2:4-dibromaniline, 2:6-dibromaniline, mesidine or 2:4:6-trimethylamiline, pseudocumidine or 2:4:5-trimethylamiline (m. p. 65° instead of 68°), diethylamiline, a-naphthylamine, β -naphthylamine, and diphenylamine.

It was to be expected that the combination between an amine and an acid would depend to a large extent on the strengths of the acid and base. So far as our investigations allow us to judge, these appear to be the only factors involved. The stereochemistry of the base or acid appears to have no direct influence on the formation of salts, and, in fact, it has been found that amines which do not combine with benzoic acid will combine with the greatest readiness with the diorthosubstituted benzoic acids examined. We can attribute this only to the increase in the strength of the acid caused by the presence of the nitro- and bromo-groups, Ostwald having shown (Zeit. phys. Chem., 1889, 3, 418) that a single bromine atom or nitro-group in the ortho-position increases the dissociation constant of benzoic acid. would be interesting to ascertain what would be the action of amines on a diortho-substituted benzoic acid such as 2:4:6-trimethylbenzoic acid, which is not a stronger acid than benzoic acid. Tertiary bases of high molecular weight, such as tribenzylamine or tripropylamine, appear to combine with diortho-substituted acids as readily as do simple amines, and, further, the two bases mesidine and pseudocumidine both combine with substituted benzoic acids, whereas 2:4dibrom- and 2:6 dibrom-aniline do not, thus indicating that the

strengths of the bases, and not stereochemical influences, are the main factors in determining whether a given acid will combine with different substituted anilines or not.

The method adopted in most cases has been to add an ethereal solution of the amine to an ethereal solution containing an equivalent amount of the acid, quantities of about 2 grams of the latter usually being employed; in many instances, a deposit of the salt was obtained immediately, or when the product was left overnight. When no such deposit was formed, the ether was distilled off and the residue extracted with a solvent in which the amine was readily soluble, but the acid practically insoluble, cold carbon bisulphide proving to be the most suitable for the purpose in nearly all cases. In those cases in which combination had not taken place, the theoretical amounts of the acid and amine were recovered, the base being obtained by evaporating the carbon bisulphide. This method does not exclude the possibility of an unstable salt having been formed, which was subsequently decomposed by the cold carbon bisulphide.

Salts were obtained from 2:4:6-trinitrobenzoic said and trimethylamine, tripropylamine, tribenzylamine, phenylamine, metabromophenylamine, metanitrophenylamine, 2:4:6-trimethylphenylamine, 2:4:5-trimethylphenylamine, phenyldiethylamine, α -naphthylamine, and β -naphthylamine.

Also from 2:4:6-tribromo-3-amidobenzoic acid and trimethylamine, tripropylamine, tribenzylamine, phenylamine, metabromophenylamine, metanitrophenylamine, phenyldiethylamine, α -naphthylamine, β -naphthylamine, 2:4:5- and 2:4:6-trimethylphenylamine.

Also from 2:4:6-tribromobenzoic acid and trimethylamine, tripropylamine, tribenzylamine, phenylamine, and metabromophenylamine. Also from metanitrobenzoic acid and trimethylamine, tribenzylamine, phenylamine, metabromophenylamine, 2:4:5- and 2:4:6-trimethylphenylamine, and from benzoic acid and phenylamine. Tripropylammonium benzoate, and phenyldiethylammonium metanitrobenzoate were only obtained as syrups. Feeble bases, like diphenylamine, and 2:4- or 2:6-dibromaniline, could not be induced to combine with strong acids like the trinitro- and tribromamido-benzoic acids, and benzoic acid itself would not combine with tribenzylamine, diethylaniline, pseudocumidine, and metabromaniline.

All the salts are readily decomposed by mineral acids, or by alkalis such as sodium hydroxide or carbonate.

In the analysis of the salts, either the nitrogen or the bromine was determined; the salts were then decomposed and the amount of organic acid estimated. As a rule, excess of sodium carbonate solution was added, and the amine extracted with ether; hydrochloric acid was then added, and the solution again extracted several times with ether. After

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drying with calcium chloride, the ethereal extract containing the acid was evaporated, and the residue weighed after exposure during one night over sulphuric acid.

EXPERIMENTAL.

Salts of 2:4:6-Trinitrobenzoic Acid.

All the salts of 2:4:6-trinitrobenzoic acid become dark when heated and then melt, evolving a considerable quantity of gas and yielding a dark red oil. The temperature at which this decomposition occurs depends on the rate at which the salt is heated. When very slowly heated, decomposition usually occurs a few degrees above the temperature at which it changes colour, although in most cases it is necessary to keep the salt at this temperature for several minutes. If more quickly heated, the temperature of fusion and decomposition may be 10° or even 20° higher.

The salts of trinitrobenzoic acid are characterised further by the fact that they yield deep red or claret solutions when heated with acetone, a green fluorescence being developed in many cases at the same time.

Trimethylammonium Trimitrobenzoate.—Trinitrobenzoic acid was warmed very gently with an excess of a 30 per cent. aqueous solution of trimethylamine; the solution turned red, but all did not dissolve. The crystalline residue and the residue obtained by evaporating the aqueous solution to dryness in a vacuum, were dried, and then washed with ether to remove any trinitrobenzoic acid. The yellowish product thus obtained melted to a dark red liquid at 119°, evolving a considerable amount of gas at the same time. On crystallisation from hot benzene, in which it is only sparingly soluble, minute crystals were obtained melting and decomposing at 118°.

0.2074 gave 31.9 c.c. moist nitrogen at 14° and 756 mm. N = 18.00. 0.6 gave 0.4856 acid. Acid = 80.9.

 $(NO_2)_8C_6H_2 \cdot COO \cdot NH(CH_8)_8$ requires N = 17.72; acid = 81.3 per cent.

The salt is insoluble in ether, very sparingly soluble in chloroform, carbon bisulphide, and light petroleum, somewhat sparingly in warm alcohol or benzene, readily in boiling water or in acetone; the solution in acetone turns deep red when heated. The same salt was obtained in a crystalline form by passing trimethylamine gas into an ethereal solution of the acid.

At the first attempt to prepare the salt by the method described, 1:3:5-trinitrobenzene was obtained in colourless plates melting at 122—123°, either when the insoluble residue or the residue left on evaporating the aqueous solution over sulphuric acid in a vacuum was crystallised from alcohol.

0.2397 gave 40 c.c. moist nitrogen at 15° and 748 mm. N = 19.61. Theory = 19.72 per cent.

Tripropylammonium Trinitrobenzoats.—Ethereal solutions of tripropylamine and the acid were employed, and an immediate precipitate of the salt was obtained; this, after recrystallisation from hot benzene, formed short, colourless prisms, which became dark at 90°, and melted and decomposed at 114°. It is readily soluble in hot water, from which it crystallises on cooling in long, celourless, prismatic needles or well-developed prisms. It is sparingly soluble in carbon bisulphide or light petroleum, but readily in alcohol, benzene, chloroform or cold acetone, the solution in acetone turning deep red on warming.

0.2653 gave 32 c.c. of moist nitrogen at 15° and 764 mm. N = 14.20. 0.7 , 0.455 acid. Acid = 65.0.

 $(NO_2)_8C_6H_2 \cdot COO \cdot NH(C_8H_7)_8$ requires $N=14\cdot 00$; acid = 64·3 per cent.

Tribenzylammonium Trinitrobenzoate.—Alcoholic solutions of tribenzylamine and the acid were employed; the salt crystallised in long, yellowish needles; it melted and decomposed at 133—134° when slowly heated, or at 142° when quickly heated. It is practically insoluble in carbon bisulphide, light petroleum (b. p. 100—120°), water, or ether, very sparingly soluble in hot alcohol, appearing to undergo partial decomposition in this solvent, sparingly in hot benzene, and readily in warm acetone, giving at first a greenish solution which, on further heating, turns deep red and exhibits a green fluorescence.

0.299 gave 26.7 c.c. of moist nitrogen at 15° and 764 mm. N = 10.51. 0.7 , 0.3325 acid. Acid = 47.5.

 $(NO_2)_3C_6\overset{..}{H}_2\cdot COO\cdot NH(C_7H_7)_3$ requires $N=10\cdot 29$; acid = 47·2 per cent.

Phenylammonium Trinitrobenzoats.—When ethereal solutions of aniline and the acid, in molecular proportion, were employed; the salt separated immediately as a white, crystalline precipitate, which melted and decomposed at 147°. It is sparingly soluble in ether, carbon bisulphide, chloroform, light petroleum, or benzene, dissolves fairly readily in warm alcohol, and readily in cold acetone, but the latter solution, when warmed, turns reddish-yellow, and finally deep red with a green fluorescence. It is moderately soluble in hot water, from which it crystallises in discoloured plates.

0.2674 gave 36.9 c.c. of moist nitrogen at 14° and 740 mm. N=15.8. 0.7 , 0.5145 acid. Acid = 73.5.

 $(NO_2)_8 C_6 H_2 \cdot COO \cdot NH_8 \cdot C_6 H_5 \ \ requires \ N = 16 \cdot 0 \ ; \ \ acid = 73 \cdot 4 \ per \ cent.$

Metabromophenylammonium Trinitrobenzoate.—Ethereal solutions of

bromaniline and the acid were used, and a copious precipitate of the salt was obtained; part was crystallised from ether and the remainder from alcohol, yellowish needles, melting and decomposing at 151°, being obtained in both cases. From the alcoholic mother liquor, impure trinitrobenzene separated in reddish coloured prisms melting at 115°, which, when recrystallised, formed flat needles insoluble in aqueous sodium carbonate and melting at 123°. The salt is moderately soluble in warm benzene, from which it crystallises in long felted needles, is practically insoluble in carbon bisulphide, very sparingly soluble in light petroleum, and fairly readily in warm alcohol.

0.2716 gave 30.2 c.c. of moist nitrogen at 15° and 748 mm. N = 12.81. 0.7 , 0.4166 acid. Acid = 59.5. $(NO_9)_8C_8H_8$. COO· NH_8 . C_8H_4 Br requires N = 13.05; acid = 59.9 per cent.

Metanitrophenylammonium Trinitrobenzoats.—Ethereal solutions of equivalent quantities of metanitraniline and the acid were mixed, and after some time a crystalline deposit was formed, which, on recrystallisation from benzene, separated in small plates. The salt is sparingly soluble in hot water, chloroform, benzene, or light petroleum, and practically insoluble in carbon bisulphide; it crystallises from benzene in small, yellow plates, from hot alcohol, in which it is fairly readily soluble, in long yellow needles, and melts and decomposes at 139°.

0.2306 gave 34.8 c.c. of moist nitrogen at 13° and 748 mm. N = 17.55. 0.7 , 0.4548 acid. Acid = 65.0. (NO₃)₃C₆H₂·COO·NH₃·C₆H₄·NO₂ requires N = 17.72; acid = 65.1 per cent.

2:4:5-Trimethylphenylammonium Trinitrobenzoats.—Equivalent quantities of pseudocumidine and the acid were separately dissolved in warm alcohol and the solutions mixed while still warm; on cooling, yellowish-brown, feathery needles were deposited from the reddish solution. The salt is very sparingly soluble in ether, benzene, carbon bisulphide, light petroleum, or chloroform, fairly readily in boiling water, crystallising from the hot solution in yellowish needles, and readily in acetone, forming a solution which, when warmed, assumes a deep red colour and a green fluorescence. When slowly heated, the salt darkens in colour at 150°, and melts and decomposes at 155°.

0.275 gave 34.7 c.c. of moist nitrogen at 14° and 737 mm. N=14.36. 0.7 , 0.456 acid. Acid = 65.1.

 $(NO_2)_3C_6H_2\cdot COO\cdot NH_3\cdot C_6H_2(CH_3)_8$ requires $N=14\cdot 29$; acid = 65.56 per cent.

 $2:4:6\cdot Trimethyl phenylammonium \ Trinitrobenzo at e. - Ethereal \ solu-$

tions of mesidine and the acid, when mixed, gave an immediate white deposit. The salt is almost insoluble in ether or carbon bisulphide, sparingly soluble in benzene, light petroleum, or boiling water, and moderately so in hot alcohol, from which it crystallises in colourless, felted needles. It changes colour at 160°, and melts and decomposes at 166.5°.

0.2646 gave 33.2 c.c. of moist nitrogen at 13° and 744 mm. N=14.5. 0.7 , 0.4574 acid. Acid = 65.34 per cent.

Phenyldiethylammonium Trinitrobenzoate.—A white, crystalline precipitate of the salt is formed immediately when ethereal solutions of diethylaniline and acid are mixed, and on recrystallisation from benzene, is obtained in the form of short, colourless, silky needles. The salt is very sparingly soluble in carbon bisulphide or light petroleum, fairly readily in hot alcohol, from which it crystallises in long, colourless prisms, and moderately in hot chloroform; it dissolves in cold acetone, but when warmed the solution turns deep red and has a green fluorescence. Boiling water dissolves it, but decomposition seems to occur as an odour of diethylaniline is observed. When heated very slowly, the salt darkens at 110°, and melts and decomposes at 115—116°; when heated somewhat more quickly, it melts at any temperature between 116° and 127°.

0.2751 gave 32.8 c.c. of moist nitrogen at 14° and 756 mm. N = 13.95. 0.7 , 0.4398 acid. Acid = 62.8. $(NO_2)_8C_6H_2\cdot COO\cdot NHEt_2\cdot C_6H_5$ requires N = 13.79; acid = 63.3 per

 $(NO_2)_3C_6H_2 \cdot COO \cdot NHEt_2 \cdot C_6H_5$ requires N = 13.79; acid = 63.3 per cent.

a-Naphthylammonium Trinitrobenzoate.—This salt, which was prepared by the method described in connection with the β -compound, is practically insoluble in ether, benzene, light petroleum, or chloroform and only sparingly soluble in boiling water, from which it crystallises in reddish needles melting and decomposing at 197°, but dissolves readily in acetone, forming a deep red solution. The solution in boiling alcohol turns deep red, and on cooling deposits deep red needles, which do not melt below 215°, and are not decomposed by sodium carbonate solution.

0.2757 gave 32.8 c.c. of moist nitrogen at 14° and 755 mm. N=13.9. 0.7 , 0.4487. Acid = 64.1.

 $(NO_2)_3C_6H_2\cdot COO\cdot N\cdot H_8\cdot C_{10}H_7 \ \ requires \ \ N=14\cdot 0 \ ; \ \ acid=64\cdot 25 \ \ per \ \ cent.$

 β -Nuphthylammonium Trinitrobenzoate.—A yellowish, apparently amorphous, precipitate is obtained when ethereal solutions of β naphthylamine and the acid are mixed. It is practically insoluble in light petroleum or carbon bisulphide, very sparingly soluble in hot benzene, chloroform, or water, but readily in boiling alcohol, the solu-

tion becoming a deep red; it is also fairly easily soluble in acetone, but the solution has the deep red colour and green fluorescence characteristic of acetone solutions of most of the trinitrobenzoates. The salt melts and decomposes at 156°.

0.294 gave 34.4 c.c. of moist nitrogen at 14° and 758 mm. N=13.73. 0.7 , 0.4479 acid. Acid = 64.0.

Salts could not be obtained by mixing ethereal solutions of the acid and of 2:4- or 2:6-dibromaniline or of diphenylamine.

Salts from 2:4:6-Tribromo-3-amidobenzoic Acid.

The acid used in these experiments was prepared by brominating metamidobenzoic acid, the amido-acid being dissolved in dilute hydrochloric acid and bromine water added to the solution until it remained permanently yellow. The precipitated tribromamido-acid was separated and purified by crystallisation from hot water; it formed long, almost colourless, prismatic needles melting at 171°.

Trimethylammonium Tribromamidobenzoate.—This salt is prepared by dissolving the acid in a slight excess of 30 per cent. aqueous solution of trimethylamine, evaporating the solution to dryness, and washing the residue well with alcohol and ether, in which the acid is readily soluble but the salt insoluble. It is practically insoluble in benzene, acetone, ether, chloroform, or light petroleum, dissolves very sparingly in alcohol, but may be recrystallised from a large quantity of boiling water, and is then obtained as flat, glistening plates which do not melt below 220°.

0.1941 gave 0.2520 AgBr. Br = 55.25.

0.7 , 0.6013 acid. Acid = 85.9.

 $NH_2 \cdot C_4HBr_3 \cdot COO \cdot NH(CH_3)_8$ requires Br = 55.42; acid = 86.37 per cent.

Tripropylammonium Tribromamidobenzoate.—When ethereal solutions of tripropylamine and the acid are mixed, an oil separates which solidifies slowly when allowed to remain, or more quickly when stirred with carbon bisulphide. This, after being washed with ether and recrystallised, separates from its solution in benzene in minute crystals, but from alcohol in well-developed, somewhat discoloured prisms melting at 141—141.5°; it is almost insoluble in ether and carbon bisulphide, and dissolves sparingly in light petroleum or benzene, but readily in warm chloroform, acetone, or alcohol.

0.2459 gave 0.267 AgBr. Br = 46.21.

0.7 , 0.506 acid. Acid = 72.3.

 $NH_2 \cdot C_6HBr_3 \cdot COO \cdot NH(C_3H_7)_8$ requires $Br = 46 \cdot 42$; acid = 72 · 3 per cent.

Tribenzylammonium Tribromamidobenzoats.—When etheres solu-VOL, LXXV. tions of the requisite quantities of tribenzylamine and the acid are mixed and allowed to remain overnight, large, somewhat discoloured prisms are deposited. These undergo partial decomposition on crystallisation: the first fraction melted at 93°, and was completely soluble in hydrochloric acid, the second formed well-developed prisms melting at 133°, and was only partly soluble in sodium carbonate or hydrochloric acid, and the final separation consisted of a small amount of the acid, and was completely soluble in sodium carbonate. The fraction melting at 133°, on analysis, proved to be the salt. It dissolves readily in cold acetone, hot alcohol, or chloroform, sparingly in benzene, ether, carbon bisulphide, or light petroleum, and is practically insoluble in water.

0.3134 gave 0.2687 AgBr. Br = 36.48.

0.7 , 0.3953 acid. Acid = 56.5.

 $NH_{\circ} \cdot C_6 HBr_8 \cdot COO \cdot NH(C_7H_7)_8$ requires Br = 36.31; acid = 56.6 per cent.

Phenylammonium Tribromamidobenzoats.—This salt is obtained immediately as a white precipitate when ethereal solutions of aniline and the acid are mixed, and crystallises from benzene in minute crystals melting at 144—145°. It is moderately soluble in boiling water, from which it crystallises in groups of minute prisms, dissolves readily in alcohol or acetone, moderately in ether, chloroform or benzene, and sparingly in carbon bisulphide or light petroleum.

0.505 gave 25.6 c.c. of moist nitrogen at 12° and 751 mm. N = 5.94.

0.2014 ,, 0.2415 AgBr. Br = 51.02.

0.7 , 0.5592 acid. Acid = 79.9.

 $NH_3 \cdot C_6HBr_3 \cdot COO \cdot NH_3 \cdot C_6H_5$ requires N = 6.0; Br = 51.39; acid = 80.1 per cent.

Metabromophenylammonium Tribromamidobenzoats.—An immediate white precipitate of this salt is obtained when ethereal solutions of metabromaniline and the acid are mixed. It crystallises from benzene in colourless needles melting at 155°, and from boiling water, in which it is moderately soluble, in colourless, felted needles melting at 155—156°; it is readily soluble in hot ether, alcohol, or acetone, moderately in warm benzene or chloroform, but only sparingly in carbon bisulphide or light petroleum.

0.2124 gave 0.2932 AgBr. Br = 58.74.

0.7 , 0.4771 acid. Acid = 68.1.

 $NH_2 \cdot C_6HBr_3 \cdot COO \cdot NH_3 \cdot C_6H_4Br$ requires Br = 58.61; acid = 68.5 per cent.

Metanitrophenylammonium Tribromamidobenzoats.—To obtain this salt, the mixed ethereal solutions of metanitraniline and the acid are evaporated and the residue crystallised from benzene. It forms

minute, canary-yellow prisms, or, when crystallised from hot water, lemon-yellow, felted needles, melts at 143°, and dissolves readily in warm alcohol or benzene and in cold ether or acetone, moderately in warm chloroform, and sparingly in carbon bisulphide.

0.2436 gave 0.2675 AgBr. Br = 46.73. 0.7 ,, 0.5098 acid. Acid = 72.8. NH₂·C₆HBr₃·COO·NH₃·C₆H₄·NO₂ requires Br = 46.87; acid = 73.0

per cent.

Phenyldiethylammonium Tribromamidobenzoate, which was obtained as an oil when ethereal solutions of the amine and acid were mixed, solidified readily when stirred with carbon bisulphide, and was purified by crystallisation from hot benzene. The salt crystallises from dilute alcohol in small prisms melting at 115—116°, dissolves readily in alcohol, acetone, or chloroform, moderately in ether, and is almost insoluble in carbon bisulphide; when boiled with water, it melts but does not dissolve, and when warmed with concentrated sulphuric acid, it gives a purple solution, which, when poured into water, forms a red precipitate.

0.2535 gave 0.2745 AgBr. Br = 46.08. 0.7 , 0.4309 acid. Acid = 71.6.

 $NH_2 \cdot C_6 HBr_3 \cdot COO \cdot NHEt_2 \cdot C_6 H_5$ requires Br = 45.9; acid = 71.5 per cent.

2:4:5-Trimsthylphenylammonium Tribromamidobenzoate is precipitated readily when ethereal solutions of pseudocumidine and the acid are mixed, and on crystallisation from alcohol is obtained in the form of minute, colourless needles. The salt is readily soluble in acetone, and moderately in chloroform, but only sparingly in benzene, carbon bisulphide, or light petroleum; it is sparingly soluble in boiling water, and crystallises from it in colourless, felted needles melting at 175°.

0.2681 gave 0.2954 AgBr. Br = 46.89. 0.7 , 0.512 acid. Acid = 73.1.

 $NH_2 \cdot C_6HBr_3 \cdot COO \cdot NH_3 \cdot C_6H_2(CH_3)_3$ requires $Br = 47 \cdot 15$; acid = 73.5 per cent.

2:4:6-Trimethylphenylammonium Tribromamidobenzoate separates immediately when ethereal solutions of mesidine and the acid are mixed, and crystallises from benzene in minute, colourless needles. It is readily soluble in alcohol, cold acetone, or hot chloroform, moderately in hot carbon bisulphide, and sparingly in hot light petroleum or water. From boiling water, it crystallises in colourless needles melting at 167—168°.

0.2694 gave 0.2976 AgBr. Br = 47.01. 0.7 n 0.5129 acid. Acid = 73.3. a-Naphthylammonium Tribromamidobenzoate is precipitated immediately on mixing ethereal solutions of the amine and acid, and when crystallised from alcohol, forms colourless crystals melting at 206°. It is almost insoluble in ether or carbon bisulphide, dissolves sparingly in light petroleum or water, more readily in hot benzene or alcohol, and very readily in acetone. From boiling water, it crystallises in feathery needles melting at 206°.

0.2438 gave 0.2649 AgBr. Br = 46.23.

0.7 , 0.5036 acid. Acid = 71.9.

 $NH_2 \cdot C_6HBr_8 \cdot COO \cdot NH_8 \cdot C_{10}H_7$ requires $Br = 46 \cdot 42$; acid = $72 \cdot 3$ per cent.

β-Naphthylammonium Tribromamidobenzoats.—Ethereal solutions of β-naphthylamine and the acid, when mixed, give an immediate white precipitate of the salt, and on crystallisation from dilute alcohol it is obtained in the form of colourless needles melting at 142—143°. It is only sparingly soluble in ether, carbon bisulphide, light petroleum, or water, but readily in acetone, chloroform, or alcohol.

0.2158 gave 0.234 AgBr. Br = 46.15. 0.7 , 0.5032 acid. Acid = 71.9.

Salts could not be obtained by mixing ethereal solutions of the acid and of 2:4- or 2:6-dibromaniline, or of diphenylamine, the theoretical amounts of the acid and amine being recovered by extraction with carbon bisulphide, thus indicating that combination had not taken place.

Salts of 2:4:6-Tribromobenzoic Acid.

The tribromobenzoic acid employed was obtained from the tribromamidobenzoic acid by eliminating the amido-group (Trans., 1895, 67, 596), and was purified by recrystallisation from benzene.

Trimethylammonium Tribromobenzoate.—To obtain this salt, the finely divided acid was dissolved in a slight excess of 30 per cent. trimethylamine solution, the solution evaporated to dryness, and the residue crystallised from alcohol. It crystallises in small, nearly colourless plates, does not melt below 220°, is insoluble in ether, and dissolves very sparingly in benzene or acetone, moderately in water, but readily in hot alcohol.

0.7 gave 0.5981 acid. Acid = 85.44. $C_6H_2Br_3\cdot COO\cdot NH(CH_3)_3$ requires acid = 85.88 per cent.

Tripropylammonium Tribromobenzoate.—This salt is obtained in well-developed, almost colourless, vitreous prisms, when ethereal solutions of tripropylamine and the acid are mixed and evaporated, and the residue crystallised from a mixture of benzene with light petroleum.

It is readily soluble in hot water, cold alcohol, benzene, chloroform, hot carbon bisulphide, or cold acetone, dissolves sparingly in light petroleum, and crystallises from carbon bisulphide in extremely well-developed prisms melting at 110°.

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0.2529 gave 0.2864 AgBr. Br = 48.19.

0.7 ,, 0.5047 acid. Acid = 72.1.

C_6H_9Br_8\cdot COO\cdot NH(C_8H_7)_8 requires Br = 47.81; acid = 71.5 per cent.
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Tribenzylammonium Tribromobenzoats.—When ethereal solutions of tribenzylamine and the acid are mixed and left for some time, a crystalline separation of the salt is obtained, which, on recrystallisation from benzene, forms short, brownish prisms. It is practically insoluble in water, but dissolves sparingly in light petroleum, moderately in carbon bisulphide, ether, or alcohol, and readily in acetone or chloroform. When heated, it appears to melt partially at about 95°, to resolidify, and then to melt at 142°.

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0.3094 gave 0.2684 AgBr. Br = 36.91.
0.7 , 0.3878 acid. Acid = 55.4.
C_6H_9Br_8\cdot COO\cdot NH(C_7H_7)_8 requires Br = 37.15; acid = 55.6 per cent.
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Phenylammonium Tribromobenzoate was obtained by triturating the acid with rather more than the required amount of aniline until a hard, solid mass was formed; this, after being well broken up, was washed with light petroleum, and crystallised from benzene. It dissolves readily in chloroform, acetone, or warm alcohol, somewhat sparingly in water, light petroleum, or ether, and is almost insoluble in carbon bisulphide. It crystallises from alcohol, light petroleum, or benzene in small, colourless plates, and melts at $141-142^{\circ}$.

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0.2012 gave 0.2504 AgBr. Br = 52.96.

0.7 , 0.5551 acid. Acid = 79.3.

C_6H_2Br_3 \cdot COO \cdot NH_3 \cdot C_6H_5 requires Br = 53.09; acid = 79.4 per cent.
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Metabromophenylammonium Tribromobenzoate was prepared by mixing ethereal solutions of metabromaniline and the acid; it is sparingly soluble in boiling water, and separates on cooling in small, colourless needles. It crystallises from dilute alcohol in small plates, dissolves readily in alcohol, acetone, or boiling chloroform, but only sparingly in carbon bisulphide or light petroleum, and melts at 141°.

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0.17 gave 0.2401 AgBr. Br = 60.1.

0.7 , 0.4728 acid. Acid = 67.5.

C_6H_2Br_3\cdot COO\cdot NH_3\cdot C_6H_4Br requires Br = 60.26; acid = 67.6 per cent.
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Salts of Metanitrobenzoic Acid.

The acid employed is obtained from Kahlbaum; it was crystallised twice from benzene, and melted at 141°.

Trimethylammonium Metanitrobenzoate was obtained by passing trimethylamine into an ethereal solution of metanitrobenzoic acid. It crystallises from water, alcohol, or benzene in colourless needles, melts at 129°, dissolves readily in cold alcohol, water, chloroform, acetone, or warm benzene, and is almost insoluble in carbon bisulphide or light petroleum.

0.2162 gave 22.8 c.c. of moist nitrogen at 10° and 752 mm. N = 12.5. 0.7 , 0.5154 acid. Acid = 73.6. $NO_{2} \cdot C_{8}H_{4} \cdot COO \cdot NH(CH_{8})_{8}$ requires N = 12.39; acid = 73.9 per cent.

Phenylammonium Metanitrobenzoate.—Small crystals of this salt separate when ethereal solutions of aniline and the acid are mixed and left for about 3 hours. The salt is readily soluble in boiling water, from which it crystallises in long, feathery needles melting at 115°; it also dissolves readily in hot alcohol, chloroform, or cold acetone, but only sparingly in carbon bisulphide or light petroleum.

0.3211 gave 29.3 c.c. of moist nitrogen at 10° and 764 mm. N = 10.98. 0.7 , 0.4469 acid. Acid = 63.8.

 $NO_2 \cdot C_6 H_4 \cdot COO \cdot NH_8 \cdot C_6 H_5 \ requires \ N = 10 \cdot 77 \ ; \ acid = 64 \cdot 2 \ per \ cent.$

Metabromophenylammonium Metanitrobenzoate is deposited when ethereal solutions of metabromaniline and the acid are mixed and allowed to remain. It is somewhat unstable, and when boiled with benzene for some time or with carbon bisulphide, is decomposed and metanitrobenzoic acid crystallises from the solutions; it may, however, be crystallised from water, dilute alcohol, chloroform, or light petroleum, and then melts at 76—77°.

0.4 gave 28.7 c.c. of moist nitrogen at 14° and 748 mm. N = 8.31. 0.7 , 0.3451 acid. Acid = 49.3.

 $NO_2 \cdot C_6H_4 \cdot COO \cdot NH_8 \cdot C_6H_4Br$ requires $N = 8 \cdot 26$; acid = 49 \cdot 26 per cent.

a-Naphthylammonium Metanitrobenzoats.—Solutions of a-naphthylamine and the acid in benzene were employed; when mixed, they turned red, and after remaining overnight deposited warty masses consisting of long, hair-like needles; on recrystallisation from benzene, the salt was obtained in slender, colourless, silky needles melting at 105—106°. It is readily soluble in cold acetone, alcohol, or chloroform, also in boiling water, but a slight odour of a-naphthylamine is observable, and on boiling with carbon bisulphide, it is decomposed, as, on cooling, crystals of metanitrobenzoic acid are obtained.

0.3 gave 23.4 c.c. of moist nitrogen at 13° and 758 mm. N = 9.19. 0.7 , 0.3746 acid. Acid = 53.5.

0.7 , 0.3236 a-naphthylamine. Base = 46.2.

 $NO_2 \cdot C_6H_4 \cdot COO \cdot NH_8 \cdot C_{10}H_7$ requires N = 9.03; acid = 53.9; base = 46.1 per cent.

 β -Naphthylammonium Metanitrobenzoate is obtained when ethereal solutions of β -naphthylamine and the acid are mixed and evaporated to dryness, and separates in long needles when benzene solutions of the amine and acid are mixed and left for a short time. It crystallises in long, pale yellow needles, melts at 119°, and is readily soluble in alcohol or cold acetone, moderately in boiling water, hot benzene, or chloroform, but only sparingly in carbon bisulphide or light petroleum.

0.3832 gave 30.3 c.c. of moist nitrogen at 14° and 748 mm. N = 9.15. 0.7 , 0.3788 acid. Acid = 53.7.

2:4:5-Trimethylphenylammonium Metanitrobenzoats.—An immediate white precipitate of this salt is obtained when ethereal solutions of pseudocumidine and the acid are mixed. It crystallises from benzene in silky needles, or from boiling water in slender needles, melts at 140—141°, and is readily soluble in cold alcohol, acetone or chloroform, or hot benzene, but very sparingly in light petroleum or carbon bisulphide.

0.2736 gave 22 c.c. of moist nitrogen at 10° and 744 mm. N=9.42. 0.7 , 0.3858 acid. Acid=55.1.

 $NO_2 \cdot C_6H_4 \cdot COO \cdot NH_8 \cdot C_6H_2(CH_8)_8$ requires $N = 9 \cdot 27$; acid = 55·3 per cent.

Metanitrophenylammonium Metanitrobenzoate is obtained in long, yellow needles when the mixed ethereal solutions of metanitraniline and the acid are allowed to evaporate. It melts at 88—89°, and is readily soluble in hot water, alcohol, benzene, chloroform, or acctone, but practically insoluble in carbon bisulphide or light petroleum.

0.25 gave 29.5 c.c. of moist nitrogen at 15° and 752 mm. N = 13.68. 0.7 , 0.3808 acid. Acid = 54.4.

 $NO_2 \cdot C_6H_4 \cdot COO \cdot NH_8 \cdot C_6H_4 \cdot NO_2$ requires $N = 13 \cdot 77$; acid = 54 · 75 per cent.

Salts could not be obtained by mixing ethereal solutions of the acid and of diethylaniline, or of tribenzylamine, and the residues left on evaporating the ether gave the theoretical amounts of acid and base on extraction with carbon bisulphide.

Salts of Benzoic Acid.

Trimethylammonium Benzoate.—Benzoic acid readily dissolved in an aqueous solution of trimethylamine, but the salt was not isolated.

Tripropylammonium Benzoate.—Benzoic acid dissolved in warm tripropylamine; when allowed to cool, the solution separated into two layers, but after several days a homogeneous syrup was obtained, which did not solidify when kept over sulphuric acid for some weeks. That combination had taken place was indicated by the fact that after a short time the mixture ceased to smell of the amine.

Phenylammonium Benzoate.—Aniline and benzoic acid do not appear to combine when their ethereal solutions are mixed and evaporated. When equivalent quantities of the amine and acid are stirred in a test-tube with a thermometer, the temperature rises from 15—30° as the mixture turns solid, thus indicating that combination has probably taken place; the resulting salt is unstable, however, and is decomposed partially when crystallised from light petroleum. This decomposition can be avoided by employing an excess of aniline in preparing the salt, or by adding 5 per cent. of aniline to the solvent. From light petroleum containing aniline, the salt crystallises in long, colourless, silky needles melting at 90°; it dissolves with the greatest readiness in cold acetone, ether, alcohol, benzene, or carbon bisulphide, and is moderately soluble in warm water or light petroleum.

0.4996 gave 28.7 c.c. of moist nitrogen at 14° and 754 mm. N = 6.51. 0.7 gave 0.3959 acid. Acid = 56.6.

 $C_6H_5 \cdot COO \cdot NH_3 \cdot C_6H_5$ requires $N = 6 \cdot 7$. Acid = 56 \cdot 7 per cent.

All attempts to isolate salts of tribenzylamine, metabromaniline, pseudocumidine, or diethylaniline with benzoic acid proved fruitless, and in each case the unaltered amine and acid were recovered in nearly theoretical quantities.

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LVIII.—A New Compound of Arsenic and Tellurium.

By E. C. SZARVASY, Ph.D., and C. MESSINGER, Ph.D.

In making an experimental investigation of the compounds which arsenic forms with the various elements of the oxygen group, a certain regularity in their properties was observed, which led to the discovery of a new telluride. The investigation, however, aimed chiefly at an elucidation of the behaviour of the compounds at high temperatures and the determination of their molecular weights by means of their vapour densities.

Up to the present time, the following compounds of arsenic with the elements of the oxygen group are known.

As_2O_5	As_2S_5	As_2Se_5	
As ₄ O ₆	As_2S_3	As_2Se_8	As_2Te_3
	As_2S_2	As_2Se_2	As ₂ Te ₂
	As ₄ S ₈	As ₂ Se	

Of these, As_4O_6 is stable at 1560°, As_2S_2 begins to dissociate at 1200° (Szarvasy and Messinger, Ber., 1897, 30, 1344), and As_2Se at about 1150° (Szarvasy, Ber., 1897, 30, 1247), the remaining oxide, sulphides, or selenides being dissociated at lower temperatures into the stable derivative of the series and oxygen, sulphur, or selenium, as the case may be.

If, now, the compounds which are most stable at high temperatures are selected from each group of those examined, we find, on comparison, a certain numerical regularity existing between their molecular weights. For simplicity's sake, the simple molecular formulæ, As₂O₂, As₂S₂, As₂Se, may be considered, and on comparing the weights of the negative components contained in the molecular weights: 30 = 48, 28 = 64, 8e = 79, the differences between them are 16 and 15 units respectively. By extending the principle, we are able to determine the formula of the tellurium compound next in the series by the following calculation: the mean value of the difference is 15.5; this, when added to 79, the preceding term, gives 94.5, a number which has to be divided by the atomic weight of tellurium in order to obtain the number of tellurium atoms capable of combining with two atoms of arsenic, 94.5/127 = 0.744. We have now to find the smallest round number the product of which, with 0.744, will give an even number of atoms. This minimum number is 4, $0756 \times 4 = 2.976$, consequently three atoms of tellurium will be in combination with As, × 4, or eight atoms of arsenic. Hence the formula of the telluride is As, Te, supposing it to be capable of existence.

We tried to prepare this compound by melting its components* in a sealed tube, in the ratio 8As: 3Te, but always with a slight excess of arsenic; by this method, we did not succeed in obtaining a homogeneous mass, as the temperature which the glass tube would bear was not high enough to transform the tellurium into vapour. In order to obtain the high temperature which was necessary, we proceeded as The mixture was well powdered and put into a tube of Jena glass, which was sealed after being filled with pure, dry nitrogen, and placed in a thick-walled tube of hammered iron (length 50 cm., bore 1.5 cm.), one end of which was sealed, the other being closed by a metal plug and strong screw. In order to counterbalance the pressure exerted in the glass tube, a few drops of alcohol were poured into the iron tube; the apparatus was then placed in a perpendicular position in a Perrot furnace and its lower end heated at 800-900°, the upper end, protruding from the furnace, being cooled in order to preserve the screw. After the experiment, the tube was allowed to cool, and on being opened a homogeneous mass of crystalline appearance was found, which mainly consisted of As, Te, mixed with more or less arsenic, according to the excess employed. This product was purified by sublimation, under pressure, in an atmosphere of nitrogen (compare Ber., 1897, 30, 1214). The telluride contained in a tube of Jena glass (about 25 cm. long and 4-6 mm. bore), which was filled with pure dry nitrogen and sealed at both ends, was placed in an inclined furnace and the whole length gently heated, the temperature of the lower part being gradually raised until the substance volatilised; crystals of the compound were found on the cooler part of the tube, the arsenic being sublimed higher up. The sublimation was repeated twice, and wholly distinct samples of the pure substance were obtained.

	Found.	As,Te, requires
Arsenic	61.45, 61.19, 61.38	61.51 per cent.
Tellurium	38·34	38.49

The compound therefore has the formula As₈Te₈, and may be called octarenotritelluride. It is insoluble in the ordinary organic and inorganic solvents, and is not attacked by hydrochloric or sulphuric acids; fuming nitric acid oxidises it to arsenic and tellurous acids.

In order to determine the molecular weight and the behaviour of the compound at high temperatures, its vapour density was determined

Te	mperature.	Density (air=1).
1.	504°	Not volatile
2.	523	26.4
3.	713	19.67
4.	916	9.98

^{*} Both the arsenic and tellurium were purified by sublimation in a vacuum.

The calculated density for a substance of the formula As₈Te₃ is 33.74. In no case was this value obtained, consequently dissociation begins as soon as the compound vaporises.

If the telluride As₈Te₃ were not a compound, the density at 523° should be 16.87, for as the constituents of a mixture are bound to each other only in a mechanical way, the arsenic would be volatilised at 523° leaving the tellurium, the temperature of vaporisation of which is about 800°. Further, as the vapour of 2As₄ occupies two volumes, the density found would have been half that calculated for the molecule As₂Te₂.

According to the data of the third and fourth experiments, dissociation is progressive, becoming complete at about 900°. This conclusion is supported by the fact that at 921°, a temperature very little higher than that attained in the fourth experiment, the vapour density of tellurium was found to be 9.82. As the density of arsenic is 10.37, the mean of these two values is 10.09, a number which agrees as well as may be expected with the density obtained in this fourth experiment.

It is proposed to determine the vapour densities of As_2Te_2 and As_2Te_3 .

Reviewing the results of these and the earlier experiments, the following regularities may be noticed.

The stability, at high temperatures, of the compounds of arsenic with other elements of the oxygen group decreases as the number of atoms of the combining elements increases. In the series As_4O_6 , As_4S_4 , As_4Se_2 , As_8Te_3 , the oxygen compound is the most stable and the tellurium compound the least stable at high temperatures. This fact is explained by the increase of the positive character of the other elements in combination.

A certain gradation is to be observed in the formation of these compounds. Arsenic burns to trioxide in air; the bisulphide is easily formed from its elements by fusion, but in the preparation of the monoselenide, pressure is required, and the telluride can only be obtained with the aid of great pressure.

The compounds belonging to the group are crystalline, and are composed, within the limits of certain temperatures, of complex molecules. The numerical relation existing between their molecular weights is remarkable, as through this the new telluride was discovered.

LIX.—The Combustion of Carbon Disulphide.

By Harold Baily Dixon and Edward John Russell.

THE first chemists to examine the combustion of carbon disulphide with any degree of accuracy seem to have been Berzelius and Marcet (*Phil. Trans.*, 1813, p. 171). They mixed oxygen with excess of carbon disulphide in a eudiometer and passed a spark; after the explosion they noticed a few drops of liquid which had condensed on the side of the tube. Water was admitted to dissolve the sulphur dioxide, and on shaking the remainder of the gas with lime water, part was absorbed, and a precipitate of calcium carbonate formed. The residue was mixed with oxygen and sparked, and then gave a precipitate with lime water showing that it had been carbon monoxide.

In 1861 (Quart. Journ. Chem. Soc., 13, 248), Playfair showed that the vapour of dry carbon disulphide was not decomposed by passing over red-hot pumice or charcoal.

In 1862 (Chem. News, 6, 3), Frankland determined its ignition point, which he stated to be 300° F., but he does not seem to have investigated the products of combustion.

Bunsen gives no method for estimating carbon disulphide vapour in his book on Gas Analysis, but in later text-books a method is given based on the assumption that when exploded with air or oxygen one volume of the vapour gives two volumes of sulphur dioxide and one of carbon dioxide. We cannot, however, find who was the originator of this method, nor indeed can we find any literature bearing on the subject until quite recent years.

In 1888 (*Phil. Trans.*, 179, 582), Brereton Baker showed that carefully dried and purified carbon disulphide explodes with oxygen just as readily as when moist.

In 1890 (Trans., 57, 625), Pedler exploded mixtures of carbon disulphide, air, and oxygen, and showed that, owing to the great amount of heat evolved, nitrogen was oxidised and the contraction observed was more than that calculated. The nitrogen oxides thus formed combine in presence of steam with some of the sulphur dioxide, and the quantity of this gas is therefore always less than it should be.

In 1890 (Brit. Assoc. Report, 776), G. S. Turpin showed that carbon disulphide underwent a "slow combustion" when heated with air or oxygen, and that a reddish-brown solid was formed by the burning of a portion of the sulphur, a lower sulphide of carbon being left.

In 1894 (Trans., 65, 616), Brereton Baker, following up his earlier experiments, stated that carbon disulphide vapour decomposes between 200° and 218°, whilst ignition does not take place below 260°. He

concludes that combustion must be preceded by decomposition into carbon and sulphur, and suggests as a possible explanation of the combustion of pure carbon disulphide that, in this nascent state, carbon and sulphur may combine with oxygen, whether dry or not.

During the past few years, different methods have been studied in this laboratory for investigating the manner in which carbon compounds burn, and it appeared of interest to apply these methods to the study of the combustion of carbon disulphide. Unfortunately, the mode of combustion appears to be a complicated one, and no simple interpretation of the results presents itself.

Purification of the Carbon Disulphide.

The best commercial carbon disulphide was allowed to stand some hours with bromine in the cold, the bromine was then removed by potash, and the carbon disulphide shaken for an hour with alkaline permanganate. After washing well with water, it was dried over calcium chloride and distilled, the first portion only being collected. Care was always taken to avoid unnecessary exposure to light. The substance thus obtained boiled very constantly at 46.8° under 772 mm. pressure.

Influence of Moisture on the Burning of Carbon Disulphide.

As already stated, Brereton Baker found that dryness does not affect the burning of carbon disulphide, and our experiments confirm this result.

Using the purest carbon disulphide we were able to prepare, we made mixtures with oxygen and nitrous oxide in varying proportions, and allowed them to dry over phosphorus pentoxide for periods varying from a fortnight to eighteen months. In every case, there was an explosion on passing a spark, and combustion was complete.

When dried mixtures of carbon disulphide and carbon monoxide with excess of oxygen were sparked, it was always found that the carbon monoxide was largely unburnt whilst the carbon disulphide burnt completely. The union of the carbon disulphide and oxygen thus occurs when the gases have been brought to a state of dryness in which carbon monoxide and oxygen are incapable of combining.

Further evidence was obtained by a comparison of the rates of explosion of wet and of dry mixtures. If moisture is necessary for combustion, the velocity of explosion in a mixture of moist gases should be greater than that in a mixture of dry gases. We found it to be less.

Mixture.	Rate of explosion of dried gases.	Rate of explosion of gases saturated with water vapour at 15°.
CS ₂ +3O ₂	1802 metres per sec.	1755 metres per sec.
CS ₂ +5O ₂	1782 ,,	1672 ,,

In no experiments have we been able to find any indication that pure carbon disulphide will not burn.

Temperature of Ignition of Carbon Disulphide.

The ignition point of carbon disulphide has been estimated at rather widely divergent temperatures. Whilst Berzelius placed it at "just above the boiling point of quicksilver," Frankland gave the ignition temperature as 300° F., or 149° C. Böttger fired carbon disulphide by molten tin at 228° C.; Brereton Baker gives the ignition point of carbon disulphide mixed with oxygen as 258—260°. Turpin states that when carbon disulphide is mixed with 10 times its volume of oxygen, the slow combustion develops into ignition at 160°; and when mixed with 10 times its volume of air it ignites at 290°.

We have endeavoured to determine the ignition point of carbon disulphide vapour and air by allowing the vapour to come into contact with a round glass flask filled with heated oil.

In the first experiments, the flask was heated by allowing a current of heated oil to circulate through the flask in which a thermometer was immersed; in the later experiments, the flask was heated externally by a flame, and the temperature allowed to fall 20—30° before the vapour was brought in contact with the glass. The liquid was contained in a porcelain basin, which was brought directly under the flask so that the surface of the liquid was about 2 inches from the bottom of the flask.

At temperatures above 260°, the vapour lit immediately or within a second or two. Below 260°, a retardation in the ignition was observed, an interval of 8—10 seconds occurring before the vapour burst into flame. When the carbon disulphide inflamed, the basin was removed and another substituted in its place.

First Series.—In one experiment, the vapour fired at 239°, in another at 240°; in two experiments, no ignition occurred at 239°. It was noticed that the inflammation began near the top of the flask.

Ignition points.	Ignition points.	Ignition points.
257°	254°	248°
246	251	245
239	247	240
	239 no igni	tion Dights by no ignition

Second Series, with a different Flack.—The oil in the flask was allowed to cool to 240°, and then the disulphide was brought beneath it. The temperature fell slowly to 236°, when the vapour inflamed. In other experiments:—

Started	at 238°	vapour	lit	at	237°
29	240	-	,,		2 38
"	238		,,		235
,,	238		,,		232

On repeating these experiments in the dark, it was observed that the vapour entered into a gentle phosphorescent combustion before inflammation, the lambent phosphorescence beginning near the top of the flask where the vapour had been longest in contact with the heated surface.

When the flasks were heated at 230°, the vapour glowed, but in no case ignited. A small pencil of light was focussed on to the thermometer from a lantern, the rest of the apparatus being in the dark. Starting at 230°, the vapour glowed vigorously for some time and the phosphorescence was visible until the temperature had fallen to 195°. When oxygen is mixed with the air and disulphide vapour, the phosphorescent flame becomes brighter, and the ignition point falls. We have ignited a mixture of oxygen and carbon disulphide below 180°. When a stream of air and oxygen is passed over carbon disulphide and the mixture flows through a glass tube heated at 200°, the "glow" can be maintained for any length of time; sulphur dioxide is formed and a reddish-brown volatile substance condenses.

Carbon disulphide, owing to this 'silent combustion,' does not exhibit a sharply-fixed temperature of ignition. It must be ranked with carbon monoxide, which, according to the experiments of Victor Meyer and Münch (Ber., 1893, 26, 2429), undergoes a silent combustion with oxygen, and therefore shows wide limits for the observed temperatures of explosion. It differs from the hydrocarbons, which, according to the same experimenters, do not exhibit quiet combination but have sharply defined temperatures of explosion.

Temperature at which Carbon Disulphide decomposes.

Whilst Playfair states that dry carbon disulphide is not decomposed by passing over red-hot pumice or charcoal, Brereton Baker, on the other hand, found that carbon was deposited when excess of carbon disulphide was exploded with oxygen, and that carbon disulphide vapour was decomposed in glass tubes at 216—218°. According to Brereton Baker's experiments, carbon disulphide decomposes below its ignition point.

We have repeated Playfair's experiment in the following way: Purified carbon disulphide was distilled through a long combustion tube packed with pieces of freshly broken porcelain surrounding a nitrogen thermometer. The glass tube was placed inside a porcelain tube, and the whole was heated until the thermometer stood at 400°. The vapour was then slowly passed through the heated tube in a current of nitrogen, and then through a flask surrounded by a freezing mixture. The condensed liquid was exceedingly clear and colourless. On examining the white porcelain after 40 c.c. of the liquid had been distilled, no trace of any deposit of carbon could be detected.

On the other hand, when a small glass bulb filled with carbon disulphide was sealed up in a glass! tube containing nitrogen, and the whole kept at 230° in an air-bath, the tube gradually became coated with a very thin, yellow deposit, similar in appearance to that produced by the prolonged action of sunlight on the vapour in a glass tube. The deposit only became visible after many hours heating.

We have often exploded excess of carbon disulphide vapour with oxygen in glass and in lead tubes, but except when a detonator of fulminate was used to fire the mixture, we have not detected any deposit of carbon in the tubes. When, however, the gases are exploded over mercury, a black deposit is often formed which we at first mistook for carbon, but it turned out to be finely divided mercury sulphide, containing free sulphur and unburnt carbon disulphide. The black deposit is volatile, dissolves in aqua regia, and the solution gives the reaction of mercuric salts. Our experiments, therefore, do not confirm the view that carbon disulphide, when exploded with oxygen, decomposes into its elements.

Decomposition of Carbon Disulphide by Light.

Some carbon disulphide was sealed up in a tube with nitrogen, and exposed during a whole summer to the action of sunlight. The interior of the tube soon became coated with a thin, dark brown film which seemed to protect the liquid from further action; at any rate, even at the end of three months, decomposition was very incomplete.

Electric light decomposes carbon disulphide, but only very slowly. Mr. Hans Renold kindly allowed us to place tubes containing carbon disulphide inside the globe of a powerful arc light in use on his premises. In one tube, oxygen was present; in another, nitrogen. After 100 hours exposure, the tubes were covered with a very faint film which could only just be seen; the liquid in the oxygen tube was unchanged in colour, that in the nitrogen tube had turned yellowish. On evaporation, both liquids yielded brown, uninviting-looking, gummy masses, which were examined under a polarising microscope.

Part of the substance showed interference colours, which were extinguished four times in a rotation of 360°; this suggested a crystalline structure, but no definite forms could be made out. The greater part of the substance, however, showed no interference colours, and so was not crystalline. The deposit would seem to consist of a gummy substance, together with some free sulphur. We have not further examined it.

Rate of Explosion of Carbon Disulphide.

The rates of explosion for different mixtures were measured by means of the apparatus described in the Bakerian Lecture for 1893 (*Phil. Trans.*, 184, 97), and, in metres per second, were as follows:

CS ₃ + O ₂ .	$CS_2 + 1\frac{1}{2}O_2$	CS ₂ + 2O ₂ .	$CS_2 + 3O_2$	CS ₂ +4O ₂ .	CS ₂ + 5O ₂ .	CS ₂ + 6O ₂ .
1584 1601	1685 1719	1752 1756 1747	1791 1810 1802	1754 1751	1710 1740 1747	1622 1657
Mean 1592	1702	1751	1802	1753	1732	1640

It will be noticed that the maximum velocity is obtained when sufficient oxygen is used to burn the carbon to carbon dioxide and the sulphur to sulphur dioxide.

Mixtures of carbon disulphide and nitric oxide will not detonate with a spark. Le Chatelier states that the mixture $CS_2 + 6NO$ requires a ball of gun cotton with potassium chlorate to detonate it.

Mixtures containing more than two volumes of carbon disulphide vapour to one of oxygen will not ignite on sparking. If more oxygen is added, a flame can be started, but it dies out after travelling a short distance, and a true explosion-wave does not appear to be set up. We have tried to set up the wave by all of the methods previously found successful in such cases, namely, by starting the explosion with

- (1) Fulminate fired in a bomb;
- (2) A mixture of hydrogen and oxygen;
- (3) A mixture of carbon disulphide with excess of oxygen; we found the explosion travelled at rates varying from 800 to 1430 metres per second. By photographing the flash, we found it to possess none of the characteristics of an explosion-wave; the flame varied in intensity and velocity, and usually died out before reaching the end of the tube.

The richest mixture that will detonate in a lead tube of 1/2 inch vol. LXXV.

diameter contains 1 volume of oxygen to 1½ volumes of carbon disulphide vapour.

With the assistance of Messrs. Jones and Bower, of this College, we took photographs of the explosion flame of carbon disulphide on a rapidly rotating film, according to the method described by Dixon Strange, and Graham (Trans., 1896, 69, 759), who were able to obtain information as to the mode of combustion of cyanogen by comparing the length of the columns of ignited gases when cyanogen was fired in a long tube with different proportions of oxygen. Our photographs show that the luminous column is much the same length, whether the disulphide is exploded with its own volume or with 5 volumes of oxygen, and so the method does not throw any light on the way in which carbon disulphide burns.

As seen by the eye, the flash has a very bright violet colour.

Method of making the Mixtures used in these Experiments.

Oxygen was saturated with carbon disulphide by being bubbled slowly through the liquid contained in a glass worm and flask. These were kept at the same constant temperature by immersion in a large water-bath of bright tin, this temperature being indicated by a delicate thermometer inserted in the flask. Since the temperature could be maintained within 0·1°, any desired mixture could be obtained by aid of the table of vapour pressures of carbon disulphide given by Ramsay and Young (Trans., 1885, 47, 653). We append some analyses of the mixtures obtained by this method.

Temp. of bath.	Barometer.	Barometer. Partial pressure		Ratio $\frac{O_g}{CS_g}$	
20mpi 01 200mi		of CS ₂ .	Calcd, from vapour pressure.	Found by analysis.	
0·3—0·5° 2·8° 4·7—4·9° 11·9—12° 17—17·1°	761 mm. 760 ,, 763 ,, 765 ,, 766 ,,	130·3 mm. 145·2 ,, 158·6 ,, 215 ,, 264·6 ,,	4·81 4·38 8·81 2·56 1·89	4·71 4·45 4·07 2·58 1·86	

The mixtures were analysed by absorbing the carbon disulphide with alcoholic potash.* In the first three cases, the gas analysis apparatus

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^{*} Carbon disulphide is only slightly absorbed by aqueous potash, but it is rapidly absorbed by a solution containing 1 part by weight of potash dissolved in 2 parts of water with a volume of pure alcohol added equal to that of the solution.

was employed; in the others, the gas was passed through alcoholic potash contained in Geissler's bulbs, and then collected over water. The increase in weight of the bulbs gave the amount of carbon disulphide present, whilst the volume of oxygen was obtained from the weight of water it displaced.

Explosion of Carbon Disulphide with a quantity of Oxygen insufficient for complete Combustion.

It has been repeatedly shown that when ethylene is exploded with its own volume of oxygen, the oxygen goes entirely to the carbon and none of it to the hydrogen. The end products are given by the equation,

$$C_2H_4 + O_2 = 2CO + 2H_2$$

In the case of carbon disulphide, however, we have never obtained products corresponding to the equation,

$$2CS_2 + O_2 = 2CO + 2S_2$$
;

the reaction is much more complicated, sulphur dioxide, carbon dioxide, carbon monoxide, and carbonyl sulphide are formed, and much carbon disulphide remains unburnt. When the oxygen was not fairly dry, hydrogen sulphide was also formed; sulphur was deposited, but no carbon.

The mixtures exploded, and the gases obtained are given in the following table:

Original gas.	SO ₃ .	CO³-	COS + CS ₂ .	co.
$\begin{array}{c} \text{CS}_2 + 2\text{O}_2 \\ \text{CS}_2 + 1\frac{1}{2}\text{O}_2 \\ \text{CS}_2 + \text{O}_2 \\ \text{100CS}_2 + 55\text{O}_2 \end{array}$	51 ·4	87·6	2·7	6·2
	89 ·9	38·7	5·2	12·9
$ \begin{array}{c} \text{CS}_2 + \text{O}_2\\ 100\text{CS}_2 + 55\text{O}_2 \end{array} $	25·4	88·7	6·2	26·1
	4·4	21·0	19·8	56

We have been able to trace no simple relationship between the products of combustion and the original gases.

The method of analysis consisted in absorbing the sulphur dioxide by means of a manganese dioxide bullet, then removing carbon dioxide with a moist stick of potash (which only acts very slowly on carbonyl sulphide), and afterwards allowing the residue to stand over dilute potash to remove carbonyl sulphide. The carbon monoxide was estimated as usual by means of acid cuprous chloride. So long as carbon disulphide was not present in large quantity, the method is fairly good, but the figures are to be taken as approximate only, especially in the last case. Unfortunately, an explosion method is

S S 2

not available for the analysis of this mixture, as two of the equations come out to be the same, so that there are more unknown quantities than equations.

In mixtures rich in carbon disulphide (for example, 100 CS₂ + 55O₂), something like 20 per cent. of the disulphide escapes combustion, and is deposited as a dew on the sides of the tube after cooling. Its identity was established in the following manner: The mixture, $CS_0 + \frac{1}{2}O_0$, was passed into a glass tube provided with a Geissler tap at one end and an ordinary tap, into which platinum wires had been fused, at the other. The tube was fixed in an air-bath with a glass top, the temperature of which was kept considerably higher than 38°, at which carbon disulphide condenses from this mixture; the excess of the mixture escaped through one limb of the Geissler tap. Before firing, the tube was carefully examined through the top of the bath to see if any liquid had deposited, but none was ever seen. A spark was then passed, and a pale blue flame travelled right down the tube. After allowing the dense fumes of sulphur to settle, a stream of dry carbon dioxide was slowly passed through the tube, and the products driven out through the second limb of the Geissler tap, where they were collected in a Meyer's stoppered phial cooled by solid carbon dioxide.

A small quantity of liquid was obtained, which had the following properties:

- (1) Highly refractive.
- (2) Very volatile and inflammable.
- (3) Gave red crystals with triethylphosphine.
- (4) In a determination of the sulphur by Carius' method,

 $0.0234 \text{ gave } 0.1402 \text{ BaSO}_4$. S = 82.2. $CS_2 \text{ requires } S = 84.2 \text{ per cent.}$

The liquid therefore was carbon disulphide.

Incidentally, we have examined the sulphur deposited in these explosions. It was isolated in two ways: (1) by cutting open the eudiometers in which the mixtures had been fired; (2) by firing the mixtures in long glass eudiometers, open at one end and having a long glass rod placed inside, on which the sulphur was very largely deposited. The latter method was very convenient, as the rod never broke, even though the eudiometer was shattered.

The sulphur was very sticky to the touch, and almost white. Under the microscope, it was seen to consist of minute globules, and when scratched with a pin it behaved like a very thick liquid, and strands of gummy matter were seen to follow the pin. If not exposed to air, the drops remain liquid for 10 or more days; exposure to the air of the laboratory, however, slowly caused them to solidify, and the solid showed distinct signs of crystallisation under the microscope. Berthelot (Compt. rend., 1857, 44, 378) states that sulphur deposited

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during the incomplete combustion of carbon disulphide is insoluble in carbon disulphide; we find, however, that much of it, though not all, is soluble, and that when the solvent is evaporated a gummy mass remains behind, which in a few hours becomes solid; this change takes place immediately on touching with ordinary sulphur.

We have already stated that we were never able to observe any deposit of carbon in our explosions; we investigated this point somewhat fully, as it constitutes one of the differences between the combustion of carbon disulphide and that of other carbon compounds.

Mixtures of carbon disulphide with from 1/2 to 5 volumes of oxygen have been fired; some were dry, others saturated with moisture at 15°; the initial pressure was varied from 250 to 1200 mm., and the tubes were sometimes short, so that the explosion-wave was not set up, and sometimes long, so that it was. Finding that some quantity of carbon disulphide remained unburnt in the explosion of mixtures containing 1/2 to 1 volume of oxygen to 1 volume of carbon disulphide, a series of experiments were made in which these mixtures were fired with mercury fulminate in a steel bomb attached to a long explosion tube. On cutting the tube into small pieces and examining the deposit, we found that for a distance of some feet it consisted of carbon and sulphur, but beyond that, to the end of the tube, it consisted of sulphur only. When carbon disulphide vapour alone is exposed to the shock of a fulminate explosion, it is decomposed into carbon and sulphur, but the decomposition dies out at a distance of a few feet from the fulminate (Dixon and Harker, Manchester Memoirs, 1892; Trans., 1896, 69, 790). The deposit of carbon in our tube would appear, therefore, to be due to the decomposition of the carbon disulphide started by the fulminate; the absence of any deposit of carbon beyond the first few feet shows that the relatively less violent explosion produced by the carbon disulphide and oxygen is not sufficient to decompose the excess of carbon disulphide into its elements.

Explosion of Carbon Disulphide with Excess of Oxygen.

When exploded in a short tube, the products found are carbon dioxide, sulphur dioxide, and sulphur trioxide, and sulphur is frequently deposited. In the explosion-wave, carbon monoxide, carbonyl sulphide, and carbon disulphide are also found. The equation:

$$CS_2 + 3O_2 = 2SO_2 + CO_2$$

never represents the change that takes place on explosion; the volume of sulphur dioxide is always less than twice that of carbon dioxide, sometimes considerably less. If only small quantities of

^{*}Possibly some subsulphide of carbon may be formed in the incomplete combustion of carbon disulphide.

nitrogen are present, some of it is invariably oxidised. A series of experiments were done to find the amount of carbon monoxide produced, and the extent to which the nitrogen was oxidised:—

Ratio of CS ₂ to O ₂ in original mixture.	Percentage of N ₂ in original mixture.	Percentage of CO in explosion products.	Percentage of N ₂ in explosion products.
1:8:12	1:46	0.26	0.84 0.84
1:3.50	1.26	0.56	0.18
1:4.09	0.68	0.48	0.18
1:4.71	1 -25	0.92 1.05	0.62
1:3.60	16.85	1·04 1·85}	19·77 } 19·94 }

In each case (except the last), the percentage of nitrogen comes out less after explosion than before, whereas, owing to the contraction after explosion, it should be greater. In the last case, there is practically no disappearance of nitrogen; 100 volumes of the original gas yield 83.41 volumes after explosion, so that the 16.85 per cent. of nitrogen should become 19.89.

These explosions were done in a coil of lead pipe 18 feet long and 1/2 inch in diameter, heated at 100° in a water-bath. The glass firing piece could not be fastened into the metal tube by Faraday's cement, since this is acted on by carbon disulphide; we therefore fastened it in with plaster of Paris, and soaked the joint with syrupy sodium silicate. We found that joints so made remained quite tight. As a lubricant for the taps, we used finely sifted plumbago, since the ordinary lubricants (tallow, &c.) absorb carbon disulphide.

In order to confirm the presence of carbon disulphide in the gases, mixtures containing 3 to 6 volumes of oxygen to one of carbon disulphide were exploded in a long lead tube heated at 100°, which could be opened at a point 5 feet from the end. By collecting the gases here, all danger of the carbon disulphide found being simply some which might have stuck to the tap was avoided. A slow stream of carbon dioxide displaced the products from the tube, and these were sent first through a flask containing lead acetate dissolved in excess of potash, and then into a flask containing triethylphosphine. A black precipitate was always obtained in the first flask, indicating carbonyl sulphide, and a red precipitate in the second, showing carbon disulphide.

^{*} It is necessary to remove sulphur dioxide before passing into triethylphosphine, as sulphur dioxide considerably impairs the delicacy of the reaction. Hydrogen sulphide (the only other gas which would give the black precipitate) was always tested for, but found to be absent.

From a long tube, some 10 c.c. of carbon monoxide were isolated from the products of explosion of a mixture of $CS_2 + 6O_2$, by allowing the products, displaced as above, to stand over potash and subsequently removing oxygen.

We find then that, even using twice as much oxygen as is theoretically necessary for complete combustion, there always remain over, in the combustion that takes place in the explosion-wave, carbon monoxide, carbonyl sulphide, and carbon disulphide.

Combustion in the Smithells' Separator.

It is quite easy to separate the carbon disulphide flame into two cones, the most convenient method being to send air dried by passing through strong sulphuric acid in towers filled with broken glass, into a glass flask of 100 c.c. capacity containing carbon disulphide and glass wool, the jet of air being allowed to play on the surface of the wool. The flask is surrounded by warm water, and the mixture of air and carbon disulphide vapour passes into the separator and burns with a flame which easily divides into two cones.

The outer cone is pale blue, and shows a bright, continuous spectrum. A piece of cold porcelain placed in the flame gives a deposit of sulphur, and sulphur is deposited in the space between the flames. No carbon is deposited. The inner cone is a greenish-grey, it shows a bright, continuous spectrum. Analysis of the interconal gases gave some very remarkable results. It was found that there was always some unchanged carbon disulphide, but only very small quantities of carbon dioxide and carbonyl sulphide. The products consist almost entirely of equal volumes of sulphur dioxide and carbon monoxide. One hundred volumes of interconal gases contain:—

80-	$CO_9 + COS + CS_9$	CO.	N.
10.32	1.96	9.58	78.14
11.30	0.74	10.32	77.64
11.3	2.5	11.7	74.5

These experiments were done at different times and in different pieces of apparatus. It is thus evident that the conditions attending a steady flame in the separator are fairly constant.

Attempts to increase the amount of carbon disulphide were unsuccessful, as also were attempts to increase that of air. In the latter case, the flame always struck back. Samples could occasionally be taken, however, before the striking back occurred, and an analysis of such a sample showed that 100 volumes of interconal gases contained:—

802.	$CO_2 + COS + CS_2$	co.	N ₂ .
16.2	2⋅5	9·1	72.2

The increased oxygen simply results in an increase in the amount of sulphur dioxide.

Conclusions.

- 1. We have not been able to obtain any evidence which would lead us to suppose that pure carbon disulphide will not explode when mixed with oxygen and sparked.
- 2. Before igniting in the air, carbon disulphide undergoes a phosphorescent combustion. The change from this to actual ignition is not sharp, and hence carbon disulphide cannot be said to have any definite ignition point. The discrepancies between the recorded determinations can thus be accounted for. In the phosphorescent combustion part of the sulphur appears to burn, leaving a sub-sulphide of carbon.
- 3. Carbon disulphide is comparatively stable when heated. At 230°, prolonged heating is necessary before the slightest decomposition is noticeable, and no change can be observed on passing it through a tube kept at 400°. It does not split up into carbon and sulphur, either when passed through a steady flame as in the Smithells' separator, or at the high temperature of the explosion-wave. Even when this decomposition is started by means of mercury fulminate, it soon dies out.
- 4. Our experiments do not confirm the view that the combustion of carbon disulphide is preceded by a decomposition into its elements.
- 5. Carbon disulphide is slowly decomposed by exposure to electric light.
- 6. The reaction that takes place when carbon disulphide is exploded with oxygen can in none of the cases observed by us be expressed by any simple equation.
- (a) When excess of oxygen is used, the products are carbon dioxide, sulphur dioxide, sulphur trioxide, sometimes free sulphur; and in the explosion-wave, carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide.
- (b) With an insufficient quantity of oxygen, the products are carbon dioxide, sulphur dioxide, carbon monoxide, carbonyl sulphide, and carbon disulphide. When the amount of oxygen is successively diminished, the quantity of sulphur dioxide falls off, and that of the carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide increases.
- (c) Even with small amounts of oxygen, there is always a division of the oxygen between the carbon and sulphur. Using a mixture, $CS_2 + \frac{1}{2}O_2$, only a portion of the carbon disulphide takes part in the reaction.
 - 7. The mixture richest in carbon disulphide that can be made to

detonate (that is, to give the "explosion-wave") by any of the methods tried by us contains 1 volume of oxygen to 1½ volumes of carbon disulphide vapour. In the other direction, the limit is not so quickly reached, and mixtures containing 6 or 7 volumes of oxygen to 1 volume of carbon disulphide vapour still detonate.

- 8. Where burnt in the Smithells' separator, the phenomena are altogether different from those observed in the explosions. The interconal gases consist of nearly equal volumes of sulphur dioxide and carbon monoxide, together with sulphur vapour and some unchanged carbon disulphide, and small quantities of carbonyl sulphide and carbon dioxide.
- 9. The combustion of carbon disulphide differs from that of other carbon compounds investigated in the following respects:—
 - (a) Carbon is not deposited.
- (b) The explosion-wave is not propagated through the mixture $2CS_2 + O_2$, and we could never realise the equation,

$$2CS_2 + O_2 = 2CO + 2S_2$$

analogous to the well-established equation,

$$C_2H_4 + O_2 = 2CO + 2H_2$$

(c) The maximum velocity of explosion is attained with the mixture, CS_2+3O_2 , that is, when sufficient oxygen is present to burn the carbon to carbon dioxide and the sulphur to sulphur dioxide.

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LX.—The Action of Nitric Oxide on Nitrogen Peroxide.

By Harold Baily Dixon and James Dysart Peterkin.

Some few years ago, the question was keenly debated whether nitrogen trioxide existed in the gaseous state. On both sides, the experimentum crucis finally appealed to was the behaviour of nitric oxide gas when mixed with gaseous nitrogen peroxide. But whilst Ramsay and Cundall, who adopted Than's method of bringing the two gases into contact over mercury, were only concerned to show that no large contraction occurred on mixing the gases, and did not aim at measuring any small alteration of volume, Lunge and Porschneff, on the other hand, used an apparatus capable of yielding very accurate results. The conclusion arrived at by both parties to the controversy was that no contraction ensued, and that, consequently, no trioxide was produced on mixing nitric oxide and nitrogen peroxide. Now it

had been shown by Lunge that the special reactions attributed to gaseous N_2O_3 were also exhibited by mixtures of excess of nitric oxide with oxygen (Trans., 1885, 47, p. 466), and by mixtures of nitric oxide with peroxide (*Zeit. anorg. Chem.*, 1894, 7, 229); the density of the vapour given off by the blue liquid, " N_2O_3 ," had also been proved not to exceed that calculated for the mixed gases. The result of these researches was therefore the abandonment of gaseous N_2O_3 by its former advocates, and the latest text-books have naturally followed suit: gaseous N_2O_3 "apparently does not exist."

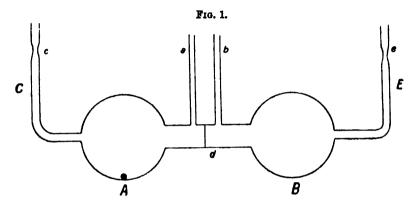
It is proverbially hard to prove a negative. In these days, when chemists recognise the importance even of traces of compounds transiently formed between reacting substances, and have discovered evidence that many well-known changes can be reversed, it could not be said to be à priori improbable that the splitting up of NoO2 should be accompanied by some slight union of its constituent gases. Such a supposition would not contradict the work of Ramsay, who has, indeed, disproved the existence of the "red fumes of nitrogen trioxide, of density 38, obtained by heating white arsenic with nitric acid," but has expressly stated that it cannot be concluded from his results that no NoO2 is present in the gaseous state. If the reaction, which may for convenience be written $N_2O_8 = NO_9 + NO$, were really reversible to a very slight extent, it would explain many of the results obtained by Lunge and others, and would, we believe, agree better with Lunge's experiments on the mixing of nitric oxide and peroxide than the conclusion Lunge himself has drawn from them.

On the Diffusion of Nitric Oxide and Nitrogen Peroxide.

In Ramsay and Cundall's well-known experiment (Trans., 1885, 47, 672), an inner tube, containing nitric oxide over mercury, was pressed against an outer tube, containing gaseous peroxide over mercury, until the inner tube broke and the two gases mixed. The two gases, being under the same pressure before mixing, would show little change of volume if they were inert to one another, but if they combined to form N₂O₃, there would be a large contraction varying with the state of dissociation of the peroxide. No alteration in the level of the mercury was observed. The experiment clearly showed that the gases had neither combined completely according to the equation $NO + NO_2 = N_2O_3$, which would have caused a contraction of one-half the volume; nor according to the equation $2NO + N_2O_4 = 2N_2O_3$, which would have caused a contraction of onethird the volume; nor in any intermediate proportion. The experiment settled the point in immediate dispute, but was obviously not designed to test the question whether any slight change of volume

occurred, such, for instance, as might result from the union of 1 per cent. of the gases.

Lunge and Porschneff (loc. cit., 237), repeated the experiment in 1894 with an ingeniously devised apparatus, in which the gases were brought together without being in contact with mercury, and which permitted small alterations of pressure to be read.



Two glass vessels, A and B (Fig. 1), each of about half a litre capacity, were separated from one another by a thin glass partition, d. Two capillary tubes, a and b, were sealed into the glass, one on each side of the thin wall. The tubes C and E, for filling the two vessels, were drawn out at c and c. A glass marble was placed in the vessel A before its neck was drawn out. The vessel B was filled with nitric oxide, and the vessel A with the vapour of the peroxide, the tubes being afterwards sealed at c and a. The vessel was then brought to the desired temperature in a water-bath, the capillary tubes opened to allow the gases to attain the pressure of the air, and then sealed again.

The partition wall was broken by making the marble fall against it and the gases were allowed to mix for half an hour. One of the capillary tubes was next connected with a petroleum manometer by a caoutchoug tube, the connected arm of the manometer being filled with carbonic acid. The end of the capillary was then broken off and the pressure observed. In one experiment at $27\cdot3-27\cdot35^\circ$, an increase in volume corresponding to 1 cm. of the oil, and in a second at 100° , an increase in volume corresponding to 1-2 cm. of the oil, were observed. This slight increase is attributed by Lunge and Porschneff to the dissociation of the peroxide on mixing with an inert gas.

Now, before we saw Lunge and Porschneff's paper, we had been led to calculate the result of mixing nitrogen peroxide with an inert gas such as nitrogen. A comparison of the vapour densities of the peroxide made by E. and L. Natanson at different pressures (Ann. Phys. Chem.,

1886, [ii], 27, 606) with the corresponding densities calculated by Willard Gibbs' theory (Am. Journ. Science, 1879, [iii], 18, 386) showed with what remarkable accuracy the variations in density could be predicted by Willard Gibbs' formula at any given temperature. If, as seemed highly probable, the mixture with an inert gas had the same effect on the dissociation of the peroxide as a direct reduction of pressure, it was evident that the mixture of nitrogen peroxide with an inert gas should have been accompanied by a noticeable increase in volume.

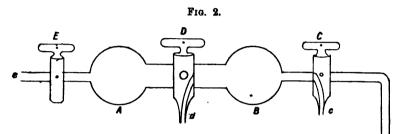
Lunge and Porschneff have not given all the data necessary to calculate the theoretical increase in volume on the assumption that the nitric oxide acted like an inert gas. But if we suppose that the barometer was at 760 mm., and the volume of the gas remained constant when the vessel was put in communication with the manometer, we can obtain a close approximation. According to Willard Gibbs, on halving the pressure (760 mm.) at 27°, the density of the peroxide would fall 6.1 per cent. In other words, the 500 c.c. of peroxide present would expand to 530 c.c., or, if the volume were kept constant, the pressure would increase to a corresponding amount. But this increase in pressure would check the dissociation, and the final effect would be an increase in pressure of 2.8 per cent. on the whole, which corresponds to an increase in volume of the peroxide from 500 c.c. to 528 c.c. Such an increase in pressure, if it had occurred in the experiment, must have been evident, for it would have moved the level in a mercury gauge through 21 mm., and the petroleum probably through 300 mm., or 30 times the observed amount.

The fact that Lunge and Porschneff found so little expansion on mixing nitric oxide and peroxide at 27° afforded some justification of the doubt we felt regarding the complete inertness of the two gases towards one another. We thought it desirable therefore to repeat the experiment, checking the results by companion experiments with inert gases, and incidentally to determine whether Willard Gibbs' dissociation formula applied to the reduction of pressure caused by mixture with an inert gas.

Apparatus employed in our Experiments.

The apparatus designed by Lunge and Porschneff, admirably adapted for carrying out a single determination, had the disadvantage of being broken in the experiment. The partition wall could not be replaced without cutting the vessel in two and submitting it to several blow-pipe operations. A repetition of an experiment under exactly the same conditions could not therefore be secured Accordingly, we had recourse to an apparatus, consisting of two vessels connected by a tap, which had been designed for a similar experiment.

namely, the determination of the change of volume in the combination of hydrogen with chlorine and oxygen (H. B. Dixon and J. A. Harker, Manchester Memoirs, 1890). Previous work with chlorine had proved that the taps could be kept tight when lubricated with damped phosphoric oxide, and preliminary trials showed us that this material also served for nitrogen peroxide, and was not sensibly acted upon.



Our apparatus is shown in Fig. 2. The vessels A and B could be put in communication by means of the large throughway of the tap D, and could be separately filled by means of taps E and C and the long tail-tap d. The pressure tube Fcould be brought into communication with the vessel B by the tap C.

The nitrogen peroxide used in these experiments was made by J. T. Cundall's method (Trans., 1891, 59, 1076).

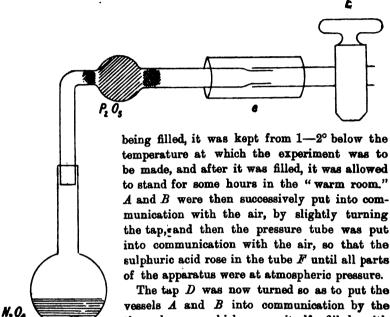
The nitric oxide was prepared by the action of nitric acid on copper, and dissolution of the nitric oxide in ferrous sulphate. The gas was kept over water in a glass holder. On passing the gas over heated copper, 145.8 c.c. gave 72.8 c.c. of nitrogen, instead of 72.9 c.c., the calculated volume.

The nitrogen, prepared by Harcourt's method, and stored over water in a glass holder, was passed over heated copper and through sulphuric acid before entering the apparatus.

The apparatus having been thoroughly cleaned, was first filled with nitrogen. The pressure tube, F, was then filled with carbonic acid and dipped into a deep vessel containing strong sulphuric acid, which was allowed to fill about half the tube. The taps were now turned off. If B was to be filled with nitric oxide, the gas was brought in through the tail-tap, c, driving the nitrogen out at d. A was filled with peroxide by attaching at e (by means of a ground glass joint and an outer paraffin joint) the end of a drying tube the other end of which was well ground into the neck of a small flask containing the liquid peroxide (Fig. 3). On warming the flask the gas, passing through the P2O5 drying tube, displaced the nitrogen in A, driving it out through the tail-tap, d. We found it convenient

to condense the peroxide, as it issued from d, by making it pass into a condenser surrounded by ice and salt. We usually passed a stream of peroxide through A for an hour, when some 30 c.c. of liquid would be found condensed in the cooled receiver. While the vessel was

Fig. 8.



sulphuric acid rose in the tube F until all parts of the apparatus were at atmospheric pressure. The tap D was now turned so as to put the vessels A and B into communication by the through-way, which was itself filled with nitrogen. The temperature and pressure of the

room being noted, the gases were allowed to diffuse for 24 hours under as constant conditions of temperature as we could secure. At the end of this time, the pressure tube was put into communication with the mixture of gases, and the level of the sulphuric acid adjusted until the whole was again under atmospheric pressure. The volumes of the gas, before and after diffusion, were thus read off at (approximately) constant pressure. In calculating the results, corrections were made for changes in the pressure of the air, and for any small changes in the temperature of the room.

Repetition of Lunge's Experiment.

A preliminary experiment, made in the manner just described, at a temperature of 27°, showed a very slight diminution in volume after the mixture of the gases.

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Volume	of	A, filled with nitrogen peroxide		122.47	c.c.
,,	,,	B, filled with nitric oxide		148.02	,,
,,	,,	through-way in tap D , filled with	h nitrogen	0.70	,,
		Total volume		271.19	c.c.
			Temp.	Pressure.	
Be	for	diffusion	27·1°	759·2	
Af	ter	33	$27 \cdot 1$	757.1	
Ind	cre	use in volume observed, 0.14 c.c.	(uncorrecte	ed).	
Co	rre	cted volume after diffusion	270	·58 c.c.	
Di	mir	ution in volume after diffusion	0	·61 ,,	

This slight alteration in the volume, less than 0.3 per cent. of the mixed gases, was in accord with the work of Lunge and Porschneff, and confirmed their statement that practically no alteration of volume occurs on mixing nitric oxide with nitrogen peroxide at 27°.

Diffusion of Nitrogen Peroxide into an Inert Gas.

The application of Willard Gibbs' formula to the data of our experiment would lead us to expect an expansion of 8.5 c.c.instead of the small contraction actually observed, if the nitric oxide acted as an inert gas.

We accordingly substituted nitrogen for the nitric oxide in the vessel B, and repeated the experiment as nearly under the same conditions as we could. The details were as follows:

	Temp.	Pressure.
Before diffusion	27·2°	738 ·8
	$27 \cdot 2$	736.1
Increase in volume observed, 7.62 c.c.	(uncorr	ected).
Corrected increase in volume after diff	usion. 6	60 c.c.

A second experiment, conducted in the same way, gave an increase in volume of 6·17 c.c.* The increase in volume found when the peroxide was allowed to diffuse into nitrogen, although less than that demanded by Willard Gibbs' formula, was sufficient to show that nitric oxide did not behave like nitrogen when mixed with the peroxide. But before any conclusions could be drawn as to the union of the nitric oxide and peroxide, it was necessary (1) to repeat the experiment so as to find out the limits of error; (2) to show that other gases, used as diluents, behaved in the same way as nitrogen, and (3) to show that nitric oxide behaved normally when allowed to diffuse into inert gases.

^{*}A later experiment, made by Lunge's method, gave an expansion of 6.2 c.c. See p. 626.

In repeating the experiments, the chief difficulty we had to overcome was the maintenance of a constant temperature. As our apparatus could not be placed in a water-bath, we used at first a large cupboard heated by small gas-jets, but as the windows had to be opened to manipulate the taps, we could not ensure the whole apparatus being at the same temperature. We finally had recourse to a small brick room in the basement of the Owens College Laboratory, built over the boiler. This room, $15 \times 10 \times 8$ feet, when closed, can be kept for many hours at a nearly constant temperature. During the preliminary adjustments and the final reading, the operator was, of course, enclosed in the room with the apparatus.

Ten experiments were made in this warm room on the diffusion of the peroxide into nitrogen. The temperature and pressure and the corrected expansion found at the end of each diffusion are given in Table I. The "expansions" are corrected in the following way.

Take, for instance, experiment 2, in which the largest change of temperature occurred. At starting, there were 271·19 c.c. of gas at 29·4° and 747·5 mm. Next day, after the diffusion, we found the volume to be 278·19 c.c. at 29·7° and 756·3 mm. But the 271·19 c.c. would have become, by reason of the change in temperature and pressure, 268·36 c.c. This latter volume expanded (owing to the dissociation of the peroxide) to 278·19 c.c.; therefore 271·19 c.c. at 29·7° and 756·3 mm. would have increased by 10·61 c.c. owing to the dissociation.

TABLE I.—Expansions found when nitrogen peroxide diffuses into nitrogen.

No. of experiment.	Temp.	Pressure in mm.	Expansion in c.c.	Differences from mean.
1	29·6°	768.2	8:30	-1.70
2 8	29.7	756.3	10.61	+0.51
8	33.2	746.8	8.06	-2.04
4	83.2	758-6	10.64	+ 0.54
5	34.8	785.0	10.40	+ 0.80
6	35.2	767.0	11.81	+1.71
4 5 6 7	35·3	728.8	11.83	+1.73
8 9	35·7	765.0	11.82	+1.72
9	36.0	761.5	8.32	-178
10	39.7	752.2	9.21	- 0.89
Mean	34·3	754	10:10	Probable error ± 0.32 c.c.

Since no regular change was found in the expansions with rise of temperature or pressure, no doubt owing to the large error of

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individual experiments, we thought it best to take the mean of all the expansions as the expansion at the mean temperature and pressure.

According to this series of experiments, when 122.47 c.c. of nitrogen peroxide, measured at 34° and 754 mm., are allowed to diffuse into 148.72 c.c. of nitrogen at constant pressure, an average expansion of 10.10 ± 0.32 c.c. is observed.

This observed expansion may now be compared with the expansion which the gas should undergo, calculated according to Willard Gibbs' theory. If 122.47 c.c. of peroxide diffuse into 148.72 c.c. of nitrogen at constant pressure (754 mm.), its volume will increase to 271.19 + v, where v is the small expansion due to dissociation. The partial pressure on the peroxide will, therefore, be

$$P = \frac{122 \cdot 47 + v}{271 \cdot 19 + v} \times 754 \dots (1)$$

Omitting v in a first approximation, the partial pressure supported by the peroxide will be 340.5 mm.

Then, from Willard Gibbs' formulæ, the densities of the peroxide at 745 mm. and at 340.5 mm. can be obtained:

$$L = \frac{3118 \cdot 6}{t + 273} + \log p - 9.451.$$

$$L_1 = \frac{3118 \cdot 6}{307} + \log 754 - 9.451 = 3.584$$

whence, by Willard Gibbs' table, $\Delta_1 = 1.603$.

Similarly,

$$L_2 = \frac{3118.6}{307} + \log 340.5 - 9.451 = 3.239,$$

and

$$\Delta_2 = 1.476.$$

From Δ_1 and Δ_2 , by multiplying by 1.589, the densities of the eroxide before and after diffusion are obtained:

$$D_1 = 2.547.$$
 $D_2 = 2.345.$

and since the volumes vary inversely as the densities,

$$V_2 = \frac{122 \cdot 47 \times D_1}{D_2} = 1399,$$

$$v = V_2 - V_1 = 10.52$$
 c.c.

Substituting this value for v in (1), we have

$$P_1 = \frac{122 \cdot 47 + 10 \cdot 52}{271 \cdot 19 + 10 \cdot 52} \times 754 = 356 \dots (2)$$

Then

$$\cdot L_8 = \frac{3118 \cdot 6}{307} + \log 356 - 9 \cdot 451 = 3 \cdot 258,$$

whence

$$\Delta_8 = 1.484$$
, and $D_8 = 2.358$.

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$$V_8 = \frac{122.47 \times 2.547}{2.358} = 132.29,$$

 $v = V_9 - V_1 = 9.82 \text{ c.c.}$

By substituting this new value in (2) we get v = 9.91 c.c.

The theoretical expansion of the peroxide by Willard Gibbs' formula is therefore 9.9~c c., which is in close agreement with the average found in our experiments, viz., 10.1~c.c.

The result of this calculation and of our experiments may be expressed in molecules, thus: In 100 molecules of the peroxide before diffusion there were 60 molecules N_2O_4 and 40 molecules NO_2 . On diffusion, 8 of the heavier molecules broke up into 16 of the lighter, giving 52 molecules N_2O_4 and 56 molecules NO_2 . An expansion of 8 per cent. of the peroxide present was thus produced.

Diffusion of Nitrogen Peroxide into other Inert Gases.

A few experiments were then made with other inert gases in the place of nitrogen. With carbonic oxide, practically the same result was obtained as with nitrogen; with the heavier gases, nitrous oxide, and carbonic acid, rather larger expansions were found. The results, calculated as before, are given in Table II. In each experiment, 122.47 c.c. of the peroxide was allowed to diffuse into 148.72 of the inert gas.

Table II.—Expansions found when nitrogen peroxide diffuses into other gases.

(A) into CO.					
No. of experiment.	Temperature.	Pressure.	Expansion in c.c.		
1 2 8	82·3° 82·8 34·1	764·8 743·0 768·1	11·41 9·50 9·38		
Mean.	83.1	758.6	10.80		
	(B) in	to N ₂ O.	· · · · · · · · · · · · · · · · · · ·		
1 2 3	33·0° 83·2 33·8	774·9 768·8 767·0	11 ·20 12 ·28 9 ·54		
Mean	33.8	770:8	11.01		

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TABLE II.—Expansions found when nitrogen peroxide diffuses into other gases—(continued).

(C)	into	CO.
(\mathbf{v})	шш	UUg.

No. of experiment.	Temperature.	Pressure.	Expansion in c.c.	
1 2	88.0°	776*2 772*4	10°97 12°06	
Mean	33.4	774:8	11.61	

These experiments, especially those with carbonic oxide, confirm the conclusion previously reached, namely, that when nitrogen peroxide diffuses into an inert gas, the dissociation it undergoes is substantially the same as, although slightly higher than, that calculated from the partial pressure by Willard Gibbs' theory.

Experiments on the diffusion of the peroxide into nitric oxide were then repeated, the vessel A being filled with the peroxide, the tap D and the vessel B being filled with nitric oxide. The results are given in Table III., which includes a few experiments (marked with an asterisk) done at a later stage:—

TABLE III.—Diffusion of nitrogen peroxide into nitric oxide.

	Temp.		Expansion in c.c.	Means.	
No. of expt.		Pressure mm.		Temp.	Expansions.
1 2 8*	27·0° 27·1 27·2	768 757 756	-1.56 -0.61 -0.10	27·2°	- 0.81
4* 5 6† 7*	27·6 28·8 30·4 31·1	745 770 758 750	+1.04/ +1.44 +1.90 +1.44	80·1	+1.29
8† 9 10 11	31·7 31·8 32·0 32·2	746 737 756 741	+1.80 +1.82 +3.54 +8.22	81 ·8	+2.38
12 13 14 15	83·0 83·3 89·5 50·8	751 751 761 761 766	+4.94 +3.95 +5.01 +9.88	32·8	+4.03

The results obtained in this series of experiments show two marked differences from those obtained under similar conditions with nitrogen.

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In the first place, the expansions are lower, in the second place, they increase fairly regularly with the temperature. These differences admit of an easy explanation on the hypothesis that, at 27°, the nitric oxide and peroxide can combine to a limited extent to form an unstable compound, which is largely dissociated at this temperature, and undergoes increasing dissociation at higher temperatures.

The only other explanations that have occurred to us are: (1) That nitric oxide behaves abnormally when mixed with inert gases; or (2) that the peroxide contained impurities (for example, nitric anhydride or oxygen) with which the nitric oxide combined; or (3) that the apparatus sometimes leaked. The first alternative could easily be tested by measuring the change of volume found when nitric oxide was allowed to diffuse into nitrogen. The following numbers were obtained in four experiments made in the same manner as before:—

Temp.	Pressure.	Expansion in c.c.	Differences from mean
16°	760	-0.41	- 0.90
29	758	-0.19	- 0.68
80	776	+1.97	+1:48
41	778	+0.60	+0.11
		Mean + 0.49	Probable error ±0.48

TABLE IV .- Diffusion of nitric oxide into nitrogen.

These numbers do not indicate that any contraction occurs on allowing nitric oxide to diffuse into an inert gas. The changes in volume observed are irregular, and are no doubt due to experimental error; the differences are not greater than those previously observed. There is nothing, then, in the physical properties of nitric oxide which accounts for its abnormal behaviour on diffusion with nitrogen peroxide.

With regard to the possibility of oxygen being present in the peroxide, some doubt might be felt, from its mode of preparation, whether the liquid might not contain some anhydride of nitric acid, which, on distilling, might yield peroxide and oxygen. To account for the abnormality observed, it would be necessary to suppose that in 100 molecules of the reputed peroxide there should be at least 4 molecules of oxygen present, which, by uniting with the nitric oxide, would show a contraction of 8 per cent.:

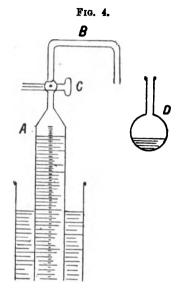
$$4O_2 + 8NO = 4N_2O_4$$

The gaseous peroxide we employed was found to be rapidly and com-

pletely absorbed by strong sulphuric acid; therefore, if any free oxygen is present, it is absorbed completely by the acid solution. Into a eudiometer, A, containing strong sulphuric acid (Fig. 4), 4 c.c. to 6 c.c.

of oxygen were introduced in several experiments. The flask D containing liquid peroxide was now attached to the bent tube B by the ground glass joint, and the air was expelled from the flask and tube by driving the vapour through the tail-tap C. Then, by means of the tap C, from 80 c.c. to 100 c.c. of peroxide were quickly passed into the eudiometer, and the absorption allowed to complete itself. The residue measured 0.1 c.c. to 0.2 c.c. more than the original oxygen, a difference which would be accounted for by the oxygen or the air contained in the through-way of the tap C.

If our peroxide really contained oxygen, it would be exceedingly unlikely that just this amount and no more should always be absorbed; we



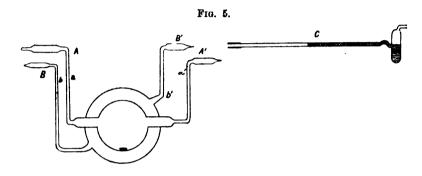
are driven, then, to the conclusion that no appreciable quantity of oxygen could be present. It is conceivable that some vapour of the anhydride N₂O₅ might exist in the peroxide, and that this might be reduced by the nitric oxide according to the equation,

$$2N_{9}O_{5} + 2NO = 3N_{9}O_{4}$$

But to account for the 8 per cent. contraction, it would be necessary to suppose that 16 per cent. of $\rm N_2O_5$ was present, a quantity which it is impossible to believe could be present in the peroxide as prepared by Lunge and by ourselves. To make sure that no nitric anhydride was present, we saturated some of our liquid peroxide with nitric oxide, and after a time submitted it to fractional distillation; the middle portion, which boiled constantly at 21.81° , was used in experiments 6 and 8, marked with \dagger in Table III. Since the results obtained did not differ appreciably from those found in the other experiments, it is evident that the anomaly cannot be accounted for by the presence of anhydride in the peroxide.

There remained, lastly, the possibility of leakage. To guard against this, we repeated the diffusion in the glass apparatus shown in Fig. 5. The inner bulb was filled with nitric oxide through the tubes A and

A', which were then sealed off; the outer bulb was filled with peroxide through the tubes B and B', which were then sealed, the tube B' being drawn off at b'. The bulbs were brought to a constant temperature in a large water-bath, and the excess of gas allowed to escape from each bulb by breaking off the ends of the tubes A and B inside a piece of rubber tubing attached to a long, narrow glass tube, previously filled with carbonic acid and supported horizontally. The bulbs could thus be left for a short time in communication with the atmosphere without the chance of any air getting in. The tubes A



and B were then sealed off at a and b, close to the surface of the water in the bath. The inner bulb was now smashed by means of a piece of glass rod enclosed in it, and the gases were allowed to diffuse for an hour while the apparatus was kept at a constant temperature. tip of the tube A' was then knicked with a file, and the horizontal gauge C, containing sulphuric acid and carbonic acid, was attached to A' by a short piece of rubber tubing. On breaking off the end of A', the movement of the liquid in the gauge gave the expansion of the gases in the apparatus. In an experiment made at 27.2° and 756 mm., the expansion found when 127 c.c. of peroxide diffused into 184 c.c. of nitric oxide was -0.1 c.c.; and in an experiment made at 27.6° and 745 mm., the expansion found when 141 c.c. of peroxide diffused into 166 c.c. of nitric oxide was +1.20 c.c. These figures are in agreement with the results previously obtained, and are recorded in Table III with a mark *, the observed expansions being reduced, for the sake of comparison, to those which would have been given by A companion experiment was also made in a similar apparatus on the diffusion of the peroxide into nitrogen. When 120 c.c. of peroxide diffused into 132 c.c. of nitrogen at 27.3° and 754 mm., the expansion produced was 6.20 c.c.

It will be observed that we have not quoted any experiments on the

diffusion of the peroxide into nitric oxide below 27°. From the figures given in Table III, it might be conjectured that at 24°, for instance, a considerable contraction would be found. This, however, is not found to be the case experimentally. The gases expand when mixed at 24°, but since a similar increase is found when the peroxide mixes with nitrogen, we attribute it to a condensation of peroxide on the glass walls when the vessel A is being filled. In several cases, we observed, with a magnifying glass, a minute dew of liquid particles on the glass, although the outside of the vessel was above the boiling point of the peroxide. This condensed liquid would evaporate on the reduction of pressure, and produce an expansion.

TABLE V.

Diffusion experiments at 24°.		Diffusion experiments at 27°.	
	Mean expansion in c.c.		Mean expansion in c.c.
Peroxide into N ₂ Peroxide into NO	+10·81 +3·74	Peroxide into N ₂ Peroxide into NO	+6.82 -0.31
Dif	ference = 6.57	Diff	erence = 6.01

The possibility that some condensation of the peroxide on the glass might affect the expansion at higher temperatures, led us to make some comparative experiments on the diffusion of a mixture of peroxide and nitrogen into nitrogen and into nitric oxide respectively.

On the Diffusion of a Mixture of Peroxide and Nitrogen into Nitrogen.

The mixtures of peroxide and nitrogen were made by diffusion in the manner previously described. The vessel A, full of the mixture, was then shut off, while B was swept out with nitrogen. After the adjustment of the temperature and of the pressure in the two vessels, the tap D was turned and the mixture allowed to diffuse into the nitrogen. The results, calculated as before, are given in Table VI. In these experiments, the through-way of the tap D was filled with the mixture.

No.	Temp.	Pressure.	Expansion in c.e.	Differences from mean.
1 2 8 4	35·5° 35·4 85·5 35·7	759 786 764 788	5·14 6·61 5·16 7·30	- 0.91 + 0.56 - 0.89 + 1.25
Mean	85.2	748	6.02	Probable error ± 0.48.

TABLE VI.—Diffusion of a mixture of peroxide and nitrogen into nitrogen.

In these experiments, the bulb A and the tap D contained a mixture which, according to the mean given in Table I, consisted of:—

52.87 Nitrogen.

47.13 Peroxide of nitrogen.

100.00

Of this mixture, 123·17 c.c. were allowed to diffuse into 148·02 c.c. of nitrogen at the average temperature 35·5° and the average pressure 748 mm. The result was an expansion of 6·05 c.c. ± 0·48.

Now the partial pressure of the peroxide before diffusion was $748 \times \frac{47.13}{100} = 352.5$ mm. Therefore, according to Willard Gibbs' theory,

$$L = \frac{3118.6}{273 + 35.5} + \log 352.5 - 9.451 = 3.182,$$

whence $\Delta = 1.454$, and D, the density of the peroxide present, = 2.311.

After the diffusion, the total volume was $271 \cdot 19 + v$, the partial pressure of the peroxide being $352 \cdot 5 \times \frac{123 \cdot 17 + v}{271 \cdot 19 + v}$. Taking the mean value found in Table VI for v, we have the partial pressure of the peroxide after diffusion

$$352.5 \times \frac{123.17 + 6.05}{271.19 + 6.05} = 164.3$$
 mm.

Therefore, according to Willard Gibbs,

$$L_1 = \frac{3118.6}{273 + 35.5} + \log 164.3 - 9.451 = 2.851,$$

whence $\Delta_1 = 1.324$, and D_1 , the density of the peroxide, = 2.104. Now since the volumes (or the number of molecules) of the peroxide vary inversely as the densities, and the original volume was

$$V = 123.17 \times \frac{47.13}{100} = 58.05$$
 c.c.,

then the volume (or number of molecules) of the peroxide after diffusion is

$$V_1 = 58.05 \times \frac{2.311}{2.104} = 63.77$$
 c.c.

Therefore, the calculated expansion undergone by the peroxide will be $V_1 - V = 5.72$ c.c.

This calculated number is in very fair agreement with the mean observed expansion, namely, 6.05 ± 0.48 c.c.

Experiments with a similar mixture of peroxide and nitrogen in the bulb A, and with nitric oxide in the bulb B, were then made. The results, calculated as before, are given in Table VII.

TABLE VII.—Diffusion q	f a mixture of nitric oxide.	•	nitrogen into

No.	Temp.	Pressure.	Expansion in c.c.	Differences from mean.
1 2 3	35·0° 35·0 86·0	767 766 750	+0.82 +1.16 +0.81	- 0·28 + 0·56 - 0·29
Mean	85*8	761	+ 0.80	Probable error ±32

On comparing the results given in Tables VI and VII, we again see that nitric oxide does not behave like an inert gas towards the peroxide.

Conclusion drawn from Diffusion Experiments.

The experimental results obtained on mixing nitric oxide with nitrogen peroxide drive us, therefore, to the conclusion that the peroxide either behaves abnormally in presence of nitric oxide, or enters into a limited combination with the nitric oxide. And since it has been shown that the peroxide behaves normally with other gases—nitrogen, nitrous oxide, carbonic oxide, and carbonic acid—we think the most probable inference is that combination occurs.

We are now investigating the action of reagents on mixtures of nitric oxide and peroxide.

If we make the assumption that the abnormal expansion of nitrogen peroxide, when mixed with nitric oxide, is due to the formation of N_2O_3 , we can readily calculate by Willard Gibbs' formula the approximate number of molecules of the several kinds which are present when

the peroxide is allowed to diffuse (1) into an inert gas, and (2) into nitric oxide. If the peroxide, when diffused into its own volume of nitrogen at 27°, expands 6 per cent., but when diffused into its own volume of nitric oxide does not alter in volume, then, on the assumption that the amount of peroxide left undissociated is the same in both cases, the numbers of molecules will be, roughly:

	I.			
	N_2O_4	NO2.	N ₂ .	Total.
Before diffusion	68	32	100	200
After "	62	44	100	206
	II.			
N_{s}	04. NO.	NO.	N ₂ O ₃ .	Total.
Before diffusion	8 32	100		200
After ,, 6	38	94	6	200

The vapour-density of the last mixture should, of course, be 3 per cent. higher than that calculated for the mixture of uncombined gases. Those experimenters who have determined the vapour-density of the gases given off from liquid N₂O₃, have found it lower than that calculated by Willard Gibbs' formula for the mixture of uncombined peroxide and nitric oxide. Thus Ramsay and Cundall found the density of the gas from the blue liquid to be 22·35 at 18°, whereas the density of the uncombined mixture should be 23·42, according to Willard Gibbs; Lunge and Porschneff found the density of their gas 27·4, whereas Willard Gibbs' formula gives for the uncombined gases 29·3.

These density determinations do not invalidate the conclusion we have come to; they only show that the quantity of gaseous N_2O_3 must be small, and that it may be necessary to modify the constant A (a function of the temperature) in Willard Gibbs' formula.

LXI.—On the Mode of Burning of Carbon. By Harold Bally Dixon.

Most works on Chemistry describe the formation of carbonic acid, in the combustion of carbon, as due to a single and direct action between carbon and oxygen; they state, or imply, that carbonic oxide is only formed by a secondary action between carbonic acid and carbon. The evidence given in support of these statements is usually (1) the burning of the diamond in oxygen to form carbonic acid without flame, and (2) the appearance of the lambent blue flame of carbonic oxide burning on the top of a red hot coke fire.

Mendeléeff (Principles of Chemistry, English edition, 1891, i, 388)

states distinctly, "the first product of combustion of charcoal is always carbonic anhydride, and not carbonic oxide." This statement is mainly founded on the experiments of Julius Lang (Zeit. physikal. Chem., 1888, 2, 168), which are, so far as I know, the only experiments professing to prove the point directly. In the same year in which Lang's experiments appeared, Brereton Baker published his researches on the combustion of carbon in dried oxygen. Neither could have been aware of the other's work, but whilst Brereton Baker, after experimenting with specially purified materials, came to the conclusion that carbonic oxide is probably first formed in the combustion of carbon, Lang decided definitely from his experiments that carbonic acid is the first product. When two investigators of admitted skill draw opposite conclusions from their experiments, it may be assumed that all the facts are not before us. I propose to examine the arguments adduced, and to add an account of some further experiments I have made in connection with this difficult question.

Lang's First Argument.

Lang experimented chiefly with purified gas-carbon, which he proved would not reduce carbonic acid at 500°. On passing oxygen through a glass tube packed with gas-carbon and heated in a furnace at 500°, he found that the products of combustion varied with the velocity of the gas-stream, the carbonic oxide formed gradually diminishing to zero.

Lang argues from his results that, since the carbonic oxide diminishes with the velocity of the gas-stream, and with a very slow stream disappears altogether, therefore the carbonic oxide found with the quicker streams was produced by the reduction of the carbonic acid owing to the local heating up of the carbon due to its oxidation to carbonic acid. When the oxygen is admitted very slowly, he thinks that each molecule of carbonic acid (produced by the direct union of its elements) may surrender to the carbon and to the walls of the vessel the extra heat due to its formation before another molecule is formed. The carbon has time to lose, by conduction and radiation, the heat thus imparted to it, and therefore remains at its original temperature of 500°, and there is consequently no possibility of a reduction of the carbonic acid to carbonic oxide.

This series of experiments, if they are exact, shows that carbonic acid is the final product when ordinary oxygen is passed slowly over carbon heated at 500°, and that carbonic acid is not reduced by the carbon at that temperature. These experiments do not directly contradict the supposition that carbonic oxide is the first product of oxidation of carbon, and that the carbonic oxide molecules so formed are further oxidised to carbonic acid, for the temperature might remain

equally stationary in whichever way the carbon was oxidised. On the supposition, however, that carbonic oxide is first formed, we should have expected that a small percentage of carbonic oxide would be found even with the slowest gas streams, because, as the oxygen was used up, the carbonic oxide molecules would be more and more surrounded by carbonic acid molecules, and some of them would be likely to escape oxidation. But, Lang argues, as no carbonic oxide is found when the stream is very slow, it is improbable that carbonic oxide is formed at all. This argument depends really on one experiment, and the answer to it is that a little carbonic oxide always is found under the conditions of this experiment; moreover, some carbonic oxide is always found when the conditions are made much more unfavourable for the reduction of carbonic acid than in Lang's experiments.

I have made some dozens of experiments on the passage of oxygen over coke heated to 500°, the melting point of lead chloride. When the stream is fairly quick, a considerable quantity of carbonic oxide is found in the products, and this quantity diminishes as the rate of flow is lessened, but in my experiments never entirely disappears. I quote the figures obtained in one set of experiments, when a mixture of 97.5 of oxygen and 2.5 of nitrogen was passed over coke at 500°.

No. of	Co	mposition o	Time of			
experi- ment.	CO ₂ .	co.	O _g ,	. N ₂ .	collecting 100 c.c.	Remarks.
1 2 3 4	80·83 87·52 96·88 96·52	16·17 9·48 1·42 0·41	0·25 0·26 0·21	2·99 2·74 1·93 2·87	3.5 min. 23 ,, 2 hours 4 ,,	Carbon dark

TABLE I.—Action of oxygen on coke at 500°.

It will be observed that a small quantity of oxygen escapes uncombined when the gas-stream is passed slowly over the coke.

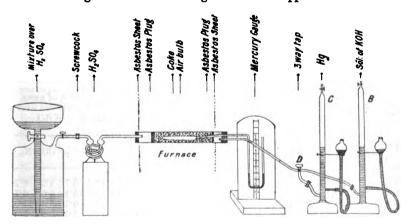
Two interpretations of these results seem possible:

- (1) That the oxygen combines directly with carbon to form carbonic acid, and that the carbonic acid is then reduced. In this case, it must be conceded that even with a very slow stream some of the carbonic acid molecules can be reduced, and therefore either the carbon or the carbonic acid is raised in temperature, in opposition to Lang's hypothesis.
- (2) That the oxygen combines directly with carbon to form carbonic oxide, and this combines with more oxygen to form carbonic acid. With the quicker gas streams some of the carbonic acid is reduced again, but with the very slow streams the carbonic oxide found either may be due to the reduction of carbonic acid or may be the direct

product of the oxidation of the carbon, these molecules diffusing into the excess of carbonic acid molecules and being cooled down before a chance of oxidation occurs.

When a stream of oxygen is passed into a tube containing heated coke, it is impossible to suppose that the portion of carbon facing the gas-stream does not get heated up, even with a slow gas-stream, for the greater part of the reaction is completed in the first 2 cm. of the coke column. It does not therefore seem admissible to say that carbonic acid cannot be reduced under these circumstances.

To make the argument conclusive, it would be necessary to show that carbonic oxide was formed under conditions in which carbonic acid could not be reduced. I do not know of any method by which such conditions could be absolutely secured, but by diluting the oxygen with an inert gas it is possible to prevent, by the cooling effect of the diluent gas, any local heating up of sensible portions of the carbon. Carbonic acid was chosen as the diluent, both on account of its high specific heat and also because its ready absorption permitted the residue to be concentrated for analysis. By calculation, it appeared probable that any mixture containing less than 7 per cent. of oxygen would have a cooling effect on the carbon; in the actual experiments, a mixture containing 8.5 per cent. of oxygen was found to have a slight cooling effect on an air-thermometer embedded in the coke. The figure shows the arrangement of the apparatus.



The tube and its contents were gradually heated until the lead chloride became pasty. The outlet of the air-thermometer was then joined to the mercury gauge, and readings were taken at intervals; when the temperature appeared steady, the gas was turned on from the holder and the flow kept at a constant rate during the experiment. The following readings of the thermometer, taken during an experiment, are quoted to show the variations of extemperature

observed; 1 mm. variation in the height of the mercury corresponds to a change of 3° in the mean temperature of the air bulb:

Time.	Mercury mm.	Gases now turned on.				
2 h. 27 m.	148.3	2 h. 52 m	147.6 mm.			
2 ,, 31 ,,	148.4	2 ,, 56 ,,	145.5 "			
2 ,, 37 ,,	148.6	3 ,, 5 ,,	145.0 ,,			
2 ,, 42 ,,	148.6	3 ,, 17 ,,	145.7 ,,			
2 ,, 47 ,,	148.7	3 ,, 25 ,,	145.8 "			
		3 ,, 31 ,,				

The products were passed into strong potash solution in B, which absorbed the carbonic acid. By turning the three-way tap, D, the gases could be diverted into the vessel C filled with mercury; about $100 \, \text{c.c.}$ were collected over mercury in each experiment. The gases were analysed over mercury, the oxygen being absorbed in some experiments by phosphorus, in others by pyrogallate, the carbonic oxide being absorbed by cuprous chloride. Fresh reagents were prepared for each determination, and blank experiments were performed with each before use.

In the following table are given (1) the composition of the gas in the holder, (2) the time of passing 100 c.c. through the coke, (3) the composition of the products collected over mercury, (4) the composition of the products collected over potash (calculated as percentages of the total volume of gas passed), and (5) the actual quantities of the products collected over potash.

TABLE II.—Effect of passing oxygen diluted with carbonic acid over coke at 500°.

of expt.	collect-				omp. of products llected over Hg.			Comp. of products collected over KHO.			C.c. of gases collected over KHO,			
No.	CO2	Og.	N ₂ .	100 c. c.	CO ₂ .	03.	co.	N ₂ .	02.	co.	N ₃ .	O ₂ .	co.	N ₂ .
1 2 3 4 5 6 7	90·8 90·8 89·0 89·7 91·0 89·6 89·9	7·7 7·7 8·4 8·5 8·1 8·4 8·3	1.5 1.5 2.6 1.8 0.9 2.0 1.8	8 m. 5 m. 7 m. 9 m. 80 m. 50 m. 65 m.	97.8 97.5 96.5 98.0 98.1 98.2	0.0 0.0 0.1 0.1 0.1 0.1	1.0 0.8 0.8 0.5 0.2 0.2	1·7 2·6 1·4 1·6 1·6	0.02 0.02 0.01		1.67 1.80 1.20	0·1 0·1 0·1 0·4 0·1 0·8	4·2 8·0 5·6 3·2 2·7 1·5 0·3	6·7 6·7 11·9 7·0 5·9 6·9 8·8

The result of this series of experiments is to show:

(1) That a gas mixture containing on the average 8 per cent. of oxygen, 90 per cent. of carbonic acid, and 2 per cent. of nitrogen, when passed over coke heated to 500°, produces a slight cooling effect;

- (2) That an appreciable quantity of carbonic oxide is found in the products of the combustion, and that this quantity is less as the rate of the gas-stream is diminished;
 - (3) That a small quantity of oxygen escapes uncombined.

Now if we accept as correct Lang's argument that, in experiments such as these, carbonic oxide can only be produced from carbonic acid when the carbon is heated locally above 600°, it is difficult to account for the carbonic oxide found except as the result of the direct union of the oxygen and carbon.

Lang's Second Argument.

But Lang's second, and perhaps more important, argument is founded on a series of experiments in which a mixture of oxygen and carbonic oxide was passed over heated carbon at different velocities.

Lang divides his experiments into three groups: 1st, at 500°, when the gas-stream is very slow, the whole of the oxygen (in two experiments) is converted into carbonic acid, and the carbonic oxide passes through the tube without being acted on. 2nd, at 500°, when the gas-stream is quicker, more carbonic oxide is found in the products than was originally present, some of the carbonic acid formed being reduced by the carbon. 3rd, at higher temperatures, or with a still quicker gas-stream, a temperature is reached at which the carbonic oxide enters into combustion.

These results, according to Lang, afford conclusive proof that in the burning of carbon the formation of carbonic acid precedes that of carbonic oxide. His argument may be thus put: "Carbonic acid may be formed slowly by the direct action of oxygen on carbon without the carbonic acid being heated up, because the carbon can conduct away the heat at the moment of formation of each molecule on its surface. But if carbonic oxide molecules were first formed, we must suppose them either to be at 500° as they leave the carbon (in which case they would be incapable of combining further with oxygen), or to retain sufficient heat to combine with oxygen (in which case the carbonic acid so produced would be so high in temperature as to bring about the combustion of the carbonic oxide originally present). But since the oxygen is wholly converted into carbonic acid under conditions in which the carbonic oxide present is not acted on, it is evident that the carbonic acid must have been formed without the intermediate formation of carbonic oxide."

This argument appears to me to be open to some criticism. For instance, it might be urged that, with a slow gas-stream, the nascent carbonic oxide molecules might combine with oxygen, and that the separate carbonic acid molecules so formed would not necessarily cause

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the inflammation of the carbonic oxide originally present, for we know that small electric sparks can be sent through explosive mixtures (for example, H_2+O) without causing inflammation, although they cause union to take place in their path. Again, the nascent carbonic oxide molecules might combine with oxygen on the surface of the carbon, for we know that one of the conditions of the union of carbonic oxide and oxygen is the presence of a conductor, for example, platinum.

But, although Lang's argument is not conclusive, it must be admitted that his view affords the easiest explanation of the experimental facts he has adduced. These facts, however, are mainly derived from two experiments only. It appeared, therefore, desirable to repeat these experiments with care, especially those with a slow gas-stream.

Repetition of Lang's Second Series of Experiments.

Mixtures containing from 75 to 80 per cent. of oxygen and 25 to 20 per cent. of carbonic oxide were collected over water; they were then passed through drying vessels of sulphuric acid and over the heated coke. The apparatus was similar to that shown in the figure on p. 633. It is unnecessary to quote the results of all the experiments (more than 100) which have been made, but I give the results of three series which are typical of the rest.

(1) Composition of Mixture.

Oxygen	76.00
Carbonic oxide	23.40
Nitrogen	0.60
	100:00

TABLE III.—Action of mixture of oxygen and carbonic oxide on coke at 450—500°.

•	Com	position of	f the prod	lucts.	Time of collect-	D. 1		
No.	CO ₂ .	co.	N ₂ .	O ₂ .	ing 100 c.c.	Remarks.		
1 2 8 4 5 6	91·8 91·2 88·5 76·8 72·2 77·4 94·8	7·3 8·1 10·9 21·8 26·3 19·9 2·8	0.9 0.7 0.6 0.8 0.8 1.3 1.2	 0.6 0.7 1.0 1.2	2 hrs. 1 hr. 35 m. 6 m. 8 m. 45 sec. 18 sec.	Carbon remained dark. ''' ''' ''' Carbon glowed. Blue flame.		

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(2) Composition of mixture.

Oxygen	74.36
Carbonic oxide	24.20
Nitrogen	1.44
	100.00

TABLE IV.—Action of mixture of oxygen and carbonic oxide on coke at 500°.

NT .	Com	position of	the prod	lucts.	Time of	
No.	CO ₃ .	co.	N ₂ .	02-	ing 100 c.c.	Remarks.
1 2 3	88.6 86.8 85.9	9·8 11·9 12·4	1.6 1.7 1.7		2 hrs. 1½ hrs. 1 hr.	Carbon remained dark.
4 5 6	75·9 84·4 92·6	22·4 13·7 5·7	1.7 1.9 1.6	=	6 m. 3 m. 20 sec.	Carbon glowed. Blue flame.

(3) Composition of Mixture.

Oxygen	76.20
Carbonic oxide	
Nitrogen	3.48
	100:00

TABLE V.—Action of mixture of oxygen and carbonic oxide on coke at 500°.

37	Com	position of	f the prod	ucts.	Time of collect-	•		
No.	CO ₂ .	co.	N ₂ .	0,	ing 100 c.c.	Remarks.		
1	92.7	2.2	5.1		9 hrs.	Carbon remained dark.		
1 2 3 4 5 6 7 8	92.0	4.7	3.3		2 hrs.	,, ,,		
3 '	91.3	5.0	3·7	_	l hr.	, ,,		
4	89.2	7:3	3.2	. —	36 m.	,, ,,		
5	81.6	15.0	3.4	, —	12 m.	, ,, ,,		
6	67.2	29.2	3.6		5 m.	,, ,,		
7	70.7	25.7	8.6	_	2½ m.	,, ,,		
8	90.7	4.6	4.0	0.7	18 sec.	Carbon glowed. Blue flame		

In all the experiments which I have made on the effect of passing a mixture of carbonic oxide and oxygen over heated coke, I find that VOL, LXXV.

amount of carbonic oxide in the products to increase as the gas-stream is made quicker until a maximum is reached, when 100 c.c. are collected in about 5 or 6 minutes. With quicker velocities, the carbonic oxide diminishes again. With a very slow gas-stream, only a small quantity of carbonic oxide escapes combustion. The results of my experiments, therefore, are entirely at variance with those of Lang's first two experiments; and if mine are correct, Lang's second argument has no foundation.

Experiments of Brereton Baker.

Brereton Baker (Phil. Trans., 1888, 179, A, 571) has proved, in a most convincing way, that carbon and oxygen, when highly purified, do not readily combine together at a high temperature. On heating purified charcoal in well-dried oxygen to redness in glass tubes, he observed no glow or scintillation (which is immediately produced in the presence of water-vapour); but on opening the vessels, part of the oxygen was found to have combined with the carbon, forming carbonic oxide and carbonic Whilst these experiments show the great influence of steam in bringing about the union of carbon and oxygen, they do not decide the question whether charcoal and oxygen would combine at all in the complete absence of moisture, or whether the carbonic oxide was formed, directly or indirectly, as the first product of oxidation. Brereton Baker states (p. 578) that the carbonic oxide found in these experiments could not have been formed by the reduction of carbonic acid, but the reason given for this statement does not appear to be valid. He shows conclusively that carbonic acid is not reduced by charcoal at 500°, but in the experiments under consideration, all the tubes are stated to have been heated "to redness." Will carbon reduce carbonic acid at a red heat when both are dried? The paper does not give us information on this point, and obviously we are not warranted in assuming that reduction will not occur under these conditions (see Mr. Brereton Baker's note).

In further experiments, Brereton Baker found that, when a stream of very carefully dried oxygen was passed over charcoal heated to redness in a glass tube, no glowing was observed, but a small quantity of carbonic acid and a considerable quantity of carbonic oxide were formed, the oxygen in all cases being in excess; the drier the substances, the less carbonic acid appeared to be produced. On the other hand, when a dried mixture of carbon and platinum black was heated to redness in oxygen, no glowing was observed, but a portion of the oxygen united with the carbon, forming carbonic acid only. Since moisture and platinum both have the power of inducing the combination of carbonic oxide with oxygen, and in the absence of these substances carbonic

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oxide is the main product formed, the results "seem to point to the conclusion that carbon burns first to carbon monoxide." These facts cannot be explained in so simple a way on the usual hypothesis that carbonic acid is the first product of oxidation.

In another series of experiments, Brereton Baker passed mixtures of oxygen and nitrogen over purified carbon heated to temperatures between 400° and 500°, and determined the proportion between the carbonic oxide and carbonic acid formed; the gases were not specially dried. He found that the proportion of carbonic oxide increased as the temperature was lowered and as the percentage of oxygen in the mixture was diminished, and argued that the carbonic oxide found in these experiments could not be due to the reduction of carbonic acid, because carbonic acid is not reduced by charcoal at 500°. This argument is, indeed, open to the criticism that, although the tube containing the carbon was only heated to 500°, the oxidation of a portion of the carbon might raise another portion to a temperature at which it would reduce carbonic acid. Nevertheless, the facts observed are certainly most easily explained on the supposition that carbonic oxide is first formed.

In continuation of Brereton Baker's work, I have found that purified charcoal does not reduce well dried carbonic acid at a temperature of about 630° (the melting point of potassium iodide). The account of the experiments by which Brereton Baker justified his statement that carbonic acid is not reduced by carbon at a red heat (loc. cit., 578) was accidentally omitted from his memoir, and in this connection he has sent me the following communication:—

"The experiments I made on dried carbon dioxide and carbon were six, and none gave any carbon monoxide. The arrangement in the last three experiments was that given in Fig. 2 in my paper (loc. cit., 575). The carbon dioxide was passed from the sulphuric acid gas-holder through flasks containing phosphorus pentoxide, so that only gas which had been standing several days over the pentoxide came in contact with the carbon. In the last experiment, the charcoal was heated to bright redness by the blowpips without producing any carbon monoxide."

This proof adds to the weight of evidence in favour of the view that carbon burns in the first instance to carbonic oxide, but whilst the arguments adduced on the other side have been shown to be invalid, it must be admitted that a decisive proof is still required.

I have to thank Mr. W. H. Yates, B.Sc., Mr. J. K. Wood, B.Sc., and Mr. Norman Smith, B.Sc., for the assistance they have given me in carrying out the experiments described in this paper.

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LXII.—A Study of the Absorption Spectra of Isatin, Carbostyril, and their Alkyl Derivatives in Relation to Tautomerism.

By Walter Noel Hartley, F.R.S., and James J. Dobbie, M.A., D.Sc.

INTRODUCTION.

MUCH uncertainty still exists with regard to the relationship between compounds described as tautomeric and desmotropic. In those cases, for example, in which a substance and two related isomeric alkyl compounds having respectively the lactam and the lactim constitution are known, it is uncertain whether the supposed parent substance has a constitution similar to that of either of the derivatives. Thus there are two methyl derivatives of isatin; the constitution of each of which has been satisfactorily determined from its chemical reactions, but there is no unquestionable evidence which proves that the constitution of isatin itself is similar to that of either of the derivatives.

It is known that the substitution of a methyl or ethyl group for an atom of hydrogen, without other alteration in the structure of the substance, merely increases the general absorption very slightly for each CH₂ added to the molecule (Phil. Trans., part I., 1879, 170, 257), that is, it slightly shortens the transmitted spectrum, but makes practically no difference in the character of the absorption; for instance, it scarcely increases its intensity, nor does it convert a general absorption into one that is selective, or vice versa. It has been explained elsewhere that the effect is to slightly retard the rate of vibration of the molecule. "The larger the molecule, the lower the rate of vibration" (Trans., 1881, 39, 165). It appeared to us that to ascertain and compare their absorption curves could scarcely fail to afford some information concerning the relationship of the constitution of such substances as isatin and carbostyril to that of their respective derivatives, whilst it seemed to offer a possible method of determining whether the constitution of the parent substance in each case is such as to admit of the derivatives being so simply related to them as the usually accepted formulæ represent.

By attacking the problem in this manner, there is the advantage gained over chemical methods that the question of the possibility of molecular rearrangement during the preparation of the derivative does not arise. Methylisatin is prepared from isatin by the action of methylic iodide on silver isatin. It is generally believed from accepted evidence that the atom of silver simply occupies the same position in the molecule as the atom of hydrogen which it has replaced and that

isatin and silver isatin have, therefore, a similar constitution. We shall show, however, that there is good ground for doubting whether any such conclusion can be justified. With the object of obtaining information on this point, we have examined the absorption spectra of isatin and carbostyril, and of their respective alkyl derivatives.

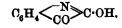
Our experiments had been completed, and conclusions drawn which merely awaited confirmation, before we had studied the recent attempts which have been made to solve this problem by chemical processes.

It is satisfactory to find that the conclusions arrived at by the examination of the absorption spectra are in complete accordance with those recently obtained by reasoning based upon purely chemical methods devised to obviate the sources of fallacy attaching to the earlier experiments.

It will be convenient to give a summary of this work before describing our experiments and the conclusions we have drawn from H. Goldschmidt and A. Meissler (Ber., 1890, 23, 253), point out that, inasmuch as some so-called tautomeric substances, such as carbostyril, when treated with alkali and alkylic haloids, give two isomeric alkyl derivatives, no conclusion as to the constitution of the parent substance can be drawn from their formation. They, likewise, hold that the action of alkylic haloids on the silver salt is untrustworthy as a guide to the solution of the problem, inasmuch as there is the possibility that the silver atom may not occupy the position of the hydrogen atom whose position is to be determined, especially as the silver derivative is usually precipitated in an alkaline solution, in which shifting of the atoms may very readily occur. Even to the method in which acid radicles are substituted for alkyl radicles, exception is taken, although it is admitted that the objections are less weighty.

The view of these authors is that, in the reactions of tautomeric substances in which electrolytes are employed, shifting of the atoms may occur. They maintain, therefore, that, in order to obtain trustworthy results, solutions of electrolytes should be excluded and only such reactions employed as give rise to no by-products which might bring about secondary changes. In their opinion, phenylic isocyanate, the reagent which they employ, fulfils these conditions.

Methylisatin, the methyl derivative of isatin which melts at 101°, and is obtained by the action of methylic iodide on silver isatin, is a lactim, since it readily undergoes saponification; whilst its isomeride, methylpseudoisatin, melting at 134°, is a lactam. On account of the direct method of preparation of methylisatin from isatin, it is generally assumed that isatin has the lactim constitution.



According to Goldschmidt and Meissler's view, the evidence of this is insufficient.

Goldschmidt and Meissler point out that, taking into account the modern views as to the nature of solutions of electrolytes, the formation of the lactim ether can be easily explained, even if we start from the lactam constitution, $C_6H_4 < \stackrel{NH}{CO} > CO$, by the formation of an intermediate potassium compound,

By the action of phenylic isocyanate on isatin, Gumpert (J. pr. Chem., [ii], 1885, 82, 283) obtained carbanilidoisatin, $C_{15}H_{10}N_2O_3$, which when treated with alkalis, passes into carbanilidoisatinic acid, $C_{15}H_{12}N_2O_4$; Goldschmidt and Meissler obtained similar results. Since carbanilidoisatin is converted by alkalis into a derivative of isatinic acid, it must be a derivative of pseudoisatin. The formula

he formulates carbanilidoisatinic acid as C_6H_4 CO·COOH
he holds to the lactim formula for isatin, explaining the formation of
the carbanilido-compound by a shifting of the atoms. It is to be
remembered, too, that Baeyer (*Ber.*, 1882, 15, 2100) explains the
formation of acetylpseudoisatin, on acetylating isatin, by a shifting of
the atoms, assuming that a molecule of acetic anhydride first unites

then, by the removal of a molecule of acetic acid, gives

Goldschmidt and Meissler, looking especially to the improbability

* See also A. Michael, J. pr. Chem., [ii], 1888, 87, 513.

888, 87, 018. Digitized by GOOGLE of phenylic isocyanate causing any shifting of the atoms, consider that the more natural explanation is that isatin itself has the lactam constitution. This conclusion is confirmed by our results, the curve of molecular absorption derived from measurements of the absorption spectra of methylpseudoisatin being practically identical with that of isatin, whilst the curve of methylisatin differs widely from both, and differs much more widely from that of isatin than the mere substitution of a methyl group for a hydrogen atom, or the addition of CH₂ to the hydrogen atom, could possibly account for.

Goldschmidt and Meissler, in the paper already referred to, show that carbostyril and lutidone behave in a similar but unexpected manner towards phenylic isocyanate, and that both compounds give off carbonic anhydride when acted on by this reagent, yielding basic products. They draw the conclusion that the two substances are similarly constituted, but this conclusion is at variance with the commonly accepted formulæ which ascribe to lutidone a ketonic and to carbostyril a phenolic consti-One or other of the formulæ must, therefore, be modified. Our experiments point to a very close similarity of constitution between carbostyril and methylpseudocarbostyril, and to dissimilarity between the constitution of both of these substances and that of methylcarbostyril. Methylpseudocarbostyril, from its reactions, is known to be a lactam, that is to say, the alkyl radicle is in direct union with the nitrogen; carbostyril itself must, therefore, have a constitution characteristic of the lactam class, a structure in character similar to that usually ascribed to lutidone. Here, again, our conclusions are in accord with those of Goldschmidt and Meissler in so far as they hold that the commonly received formula either of carbostyril or of lutidone must be altered. Knorr (Annalen, 1896, 293, 81) also arrives at the conclusion that carbostyril is to be regarded as a lactam. and not as a lactim.

We now proceed to give a detailed account of the preparation of the various substances and of the examination of their absorption spectra. All the substances examined were prepared twice over, except methylcarbostyril, and several series of photographs of each preparation were taken and carefully compared, cadmium electrodes being used as the source of light in this case, although we usually employ lead—cadmium and tin—cadmium alloys.

EXPERIMENTAL.

Carbostyril.—The preparation employed, obtained from Schuchardt, of Görlitz, was recrystallised many times from alcohol until its melting point was constant. It crystallised in fine, silky needles which melted at 195—196°.

Methylpseudocarbostyril. - To prepare this, 1 part of carbostyril was dissolved in 12 times the weight of methylic alcohol, and water added to the solution until the carbostyril just remained dissolved while the solution was hot. To the cooled solution, rather more than the calculated quantity (1 mol.) of methylic iodide was added, and then a concentrated solution of sodium hydroxide (1 mol.) in small quantities at a time, and the solution boiled, using a reflux condenser. until the alkaline reaction disappeared. The solution was next made strongly alkaline with sodium hydroxide, and the methylpseudocarbostyril extracted by shaking many times with chloroform in a separating funnel; the chloroform was distilled off, and the residue repeatedly extracted with small quantities of boiling light petroleum. From the light petroleum, the methylpseudocarbostyril crystallised in tufts of beautiful, colourless needles. After being crystallised several times from light petroleum, its melting point was 71° (Ber., 1887, 20. 2011).

Methylcarbostyril.—Methylcarbostyril was prepared by the action of methylic iodide on silver carbostyril; this was obtained by adding ammonia to a hot aqueous solution of carbostyril which had been mixed with the necessary quantity of silver nitrate. The white, amorphous precipitate of silver carbostyril is easily soluble in excess of ammonia, and from the ammoniacal solution it may be obtained in the crystalline form. The silver carbostyril was carefully dried over sulphuric acid, and heated in sealed tubes with excess of methylic iodide at 70—80°, the heating being continued for 6—7 hours. The methylcarbostyril, obtained on treating the product with alcohol and evaporating, was distilled over in a current of steam, separated from the water, and dried; it was then fractionated under a pressure of about 500 mm. The boiling point, at the ordinary presssure, is 247—249° (Ber., 1881, 14, 1916).

Although only one preparation of methylcarbostyril was made, the corresponding ethyl derivative was prepared and the absorption spectra examined, yet it gave a practically identical absorption curve. It was, therefore, considered unnecessary to duplicate these experiments.

Isatin.—The isatin, obtained from Schuchardt, of Görlitz, was recrystallised from alcohol until the melting point was constant, namely, 203.5°; the melting point given by Baeyer is 201°.

Methylpseudoisatin.—The preparation of this substance may be conveniently divided into four stages.

I. Preparation of methylphenylhydrazinepyroracemic acid.

- II. Preparation of methylindolecarboxylic acid.
- III. Preparation of methyldibromoxindole.
- IV. Conversion of methyldibromoxindole into methylpseudoisatin.
- I. Preparation of Methylphenylhydrazinepyroracemic Acid.—Twenty grams of methylphenylhydrazine dissolved in very dilute hydrochloric acid was treated with the equivalent quantity of pyroracemic acid and the crystalline mass of methylphenylhydrazinepyroracemic acid which separated was collected with the aid of the pump and washed with cold water.
- II. Preparation of Methylindolecarboxylic Acid.—The finely powdered methylphenylhydrazinepyroracemic acid was warmed on the waterbath with 5 times its weight of a 10 per cent. solution of hydrochloric acid, and the methylindolecarboxylic acid which separated in yellowish needles, was collected with the aid of the pump, washed with water, and recrystallised several times from alcohol, when it melted at 212°.
- III. Preparation of Methyldibromoxindols.—One part of the methylindolecarboxylic acid, dissolved in a dilute solution of sodium hydroxide, was gradually added to a solution containing $4\frac{1}{2}$ parts of bromine, 200 parts of water, and the equivalent quantity of sodium hydroxide, the mixture being well stirred and cooled. The bromide, which separated in very fine, yellow crystals, was crystallised several times from alcohol, from which it always separated in yellowish needles melting at 201°. According to Fischer and Hess (Ber., 1884, 17, 559), methyldibromoxindole crystallises in "clear tabular crystals" which melt at 204°, but we never obtained it in this form.
- IV. Preparation of Methylpseudoisatin from Methyldibromoxindole.—For the conversion of the methyldibromoxindole into methylpseudoisatin, we followed Colman's method (Annalen, 1888, 248, 116) in preference to that of Fischer and Hess (loc. cit.). The methyldibromoxindole was boiled with 30 times its weight of water for 2—3 hours, using a reflux condenser. The hot solution, filtered from some resinous matter, deposited the methylpseudoisatin in beautiful, red needles which, after recrystallisation from water, melted constantly at 132—133° (Fischer and Hess, loc. cit.).

Methylisatin.—The preparation of this derivative requires special precautions on account of its instability; the method followed was that given by Baeyer (Ber., 1882, 15, 2093). Five grams of finely powdered isatin were suspended in ice-cold water containing pieces of ice, and dissolved by adding a solution of sodium hydroxide also cooled to 0°; the calculated quantity of silver nitrate was now added in an ice-cold solution, and the dark red precipitate of silver isatin rapidly collected with the aid of a pump. The silver isatin after being washed

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first with water, and then with alcohol to remove any unaltered isatin, was dried over strong sulphuric acid for three days, finely powdered, and treated in a flask with excess of methylic iodide; the semi-solid mass obtained on allowing the corked flask to remain for 48 hours was repeatedly extracted with small quantities of hot benzene, and the benzene solution diluted with an equal volume of light petroleum, which caused a small quantity of tarry matter to separate. filtered solution was then evaporated to dryness on the water-bath, and the residue dissolved in the smallest possible quantity of hot benzene; on cooling, it deposited the methylisatin in prisms of a blood red colour, which, after recrystallisation from benzene, melted at 99-101° (Baeyer, Ber., 1882, 15, 2093). Methylisatin is unstable both in the solid state and in alcoholic solution. When freshly prepared, it has a sharp melting point and a blood red colour, but after it has been kept for some time the colour changes to brick red and the melting point is no longer sharp. It was, therefore, found necessary to photograph this substance immediately after its preparation.

We now proceed to give a general description of the spectra examined. Oscillation frequencies are indicated by $^1/\lambda$ and wavelengths by λ .

DESCRIPTION OF THE SPECTRA OF THE SUBSTANCES INVESTIGATED.

Carbostyril.

General description of the spectra.—There is a total absorption of all rays beyond $^{1}/\lambda$ 2700, until the dilution is 1 milligram-mol. of the substance in 500 c.c. of liquid with 5 mm. of thickness, when the rays extend to 2770.

At a thickness of 3 mm., an absorption band becomes visible, which continues to 1 milligram-mol. in 2500 c.c. with a thickness of 1 mm.

With 2 mm. of liquid containing 1 milligram-mol. in 500 c.c., the absorption band lies between $^{1}/\lambda$ 2900 and 3300, the rays being transmitted then as far as $^{1}/\lambda$ 3500, after which there is total absorption.

When the absorption band has almost disappeared, the continuous spectrum extends to $^{1}/\lambda$ 4000, and the liquid in a layer of 2 mm. then contains 1 milligram-mol. in 2500 c.c.

Methylpseudocarbostyril.

General description of the spectra.—There is a total absorption of all rays beyond $^1/\lambda$ 2680 in from 25 mm. to 15 mm. of liquid; this extends as far as 2780 with 1 mm. of liquid containing 1 milligram-mol. in 100 c.c. There is an absorption band from $^1/\lambda$ 2850 to 3370, with 3 mm. of liquid containing 1 milligram-mol. in 500 c.c., and a very feeble transmission of rays from 3370 to 3500. This absorption band

is distinctly seen down to a dilution of 1 milligram-mol. in 2500 c.c. with 2 mm. of liquid, the continuous rays then extend to about 4050.

It will thus be seen that the spectrum curve very closely resembles that of carbostyril, the general absorption being slightly increased, which is the usual effect when methyl takes the place of hydrogen or CH_2 is added to the molecule.

Methylcarbostyril.

General description of the spectra.—All rays are transmitted to $^{1}/\lambda$ 3000 by 1 milligram-mol. of substance in 500 c.c. and 5 mm. of liquid. The rays beyond are all absorbed.

Through a layer of 3 mm., the rays extend to $^{1}/\lambda$ 3050, and from this point to 3350 there is an absorption band, beyond which the rays are transmitted to 3500. The band is very feeble with 5 mm. of liquid containing 1 milligram-mol. in 2500 c.c., and it is only just visible with 4 mm. The absorbed rays lie between 3000 and 3050, beyond this is an imperfectly transmitted continuous spectrum to about 3800.

The chief differences between these spectra and those of the parent substance, carbostyril, is the great extent of the transmitted rays and the different position of the absorption band as well also as its less persistent character or intensity.

Isatin.

General description of the spectra.—There is a very strong absorption band extending from about $1/\lambda$ 1920 to 2780, that is to say, from the green into the ultra-violet, red, yellow, and green rays are transmitted. This absorption continues with 10 mm. of liquid containing 1 milligrammol. in 100 c.c. With 5 mm., there is a very feeble transmission of rays between 2780 and 3000, and with 4 mm., the transmitted rays are a little stronger, but there is total absorption beyond. With 3 mm. of liquid containing 1 milligram-mol. in 100 c.c., rays are very feebly transmitted from ½ 2000 to 2170, a second absorption band occurs as far as 2780, the rays are transmitted from 2780 to 3070, beyond which there is total absorption. This second absorption band continues, although much enfeebled, with 4 mm. of liquid containing 1 milligram-mol. in 500 c.c. Beyond 3170, there is total absorption to about 1/A 3630. It continues between 3200 and 3630 with 2 mm. of liquid containing 1 milligram-mol. of substance in 500 c.c. There is total absorption beyond 3900.

Methylpseudoisatin.

General description of the spectra.—A very strong absorption band extends from ¹/λ 1920 in the green to the very strong rays between

 $^{1}/\lambda$ 2740 and 2900 in all thicknesses of liquid from 25 mm. down to 5 mm. containing 1 milligram-mol. in 100 c.c. All rays beyond 2900 are totally absorbed.

With layers of 4 mm. and 3 mm., there is a strengthening of the transmitted rays between $^1/\lambda$ 2740 and 2970, but a total absorption beyond. With 2 mm. and 1 mm. of liquid, the absorption of rays less refrangible than 2740 is much diminished, that is to say, the band is weakened hereabouts. With layers of 5, 4, and 3 mm. of liquid containing 1 milligram-mol. in 500 c.c., there is nothing transmitted beyond $^1/\lambda$ 3030, except the very strong line at 3600.

There is a second very strong absorption band beyond this line until we get to a layer of 4 mm. of 1 milligram-mol. in 2500 c.c., when the rays between 3600 and 3840 are feebly transmitted, and there is only a very feeble transmission of rays beyond, lying between 4250 and 4400, and so gradually the absorption diminishes.

Methylisatin.

General description of the spectra.—With 1 milligram-mol. of substance in 100 c.c., there is a total absorption beyond 1920 in the green with 25, 20, 15, 10, and 5 mm. of liquid, with, however, in the last case, a very feeble transmission of rays commencing between $^{1}/\lambda$ 2000 and 2170. With 3 mm. of liquid, it is evident that a very strong absorption band lies between $^{1}/\lambda$ 2180 and about 3350, where the rays are very feebly transmitted, all beyond 3470 being totally absorbed. This absorption band gradually diminishes in intensity but more rapidly on the part of the rays of greater oscillation frequency than is the case with those lying between $^{1}/\lambda$ 2270 and 2870. For instance, 2 mm. of liquid containing 1 milligram-mol. in 500 c.c. absorb the rays between 2600 and 2770. Total absorption is seen beyond 2600.

The spectrum curves of isatin and methylpseudoisatin are very similar, but that of methylisatin is quite different. The former each show two absorption bands similar in position and intensity, whilst the latter exhibits but one.

Conclusions.

Accordingly, we conclude as regards carbostyril and its derivatives, that carbostyril and the so-called methylpseudocarbostyril are of similar constitution, the latter being the true methyl derivative of the former. The same may be said of the substance termed ethylpseudocarbostyril; it is the normal ethyl derivative. The so-called "methylcarbostyril" differs from carbostyril in constitution, and is not its true alkyl derivative.

From the similarity of the curves of molecular absorption of carbostyril and methylpseudocarbostyril, we infer that if, as is

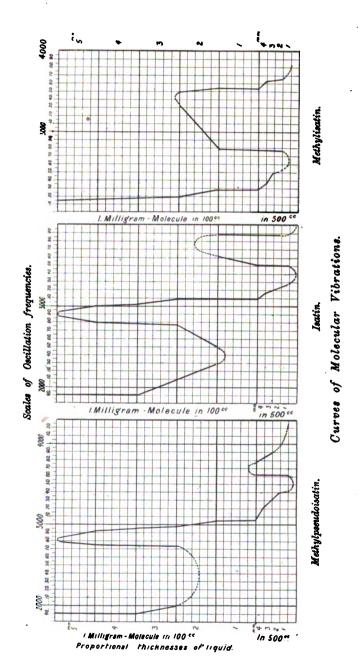
usually admitted, the latter possesses the lactam constitution, this constitution must also be assigned to carbostyril.

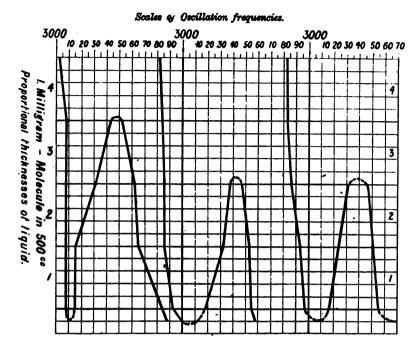
In the same way, isatin and the so-called methylpseudoisatin are of similar constitution, and isatin is, therefore, a lactam. The so-called methylisatin is not the true alkyl derivative of isatin, seeing that the curves of molecular absorption of the two substances are totally different.

ILLUSTRATIONS.

As the descriptions of the spectra and the measurements afford no idea of the photographs, it became necessary to present a graphic representation of the results. The method of drawing the curves is that which was first described in 1885 (Hartley, Trans., 1885, 47, 685; 1887, 51, 153-201. See notes to the plates, and also Trans., 1888, 53, 642). From ten to fifteen spectra are successively photographed on one plate, each representing the absorption spectrum of the same solution, such as contains 1 milligram-mol. in 100 c.c. placed in cells of different thicknesses, so as to give layers of liquid of 15, 10, 5, 4, 3, 2, 1 millimetres thick. The solution is then diluted to five times its volume, so that a milligram-mol. is contained in 500 c.c., and again photographed on another plate in cells 5, 4, 3, 2, 1 millimetres thick. The absorption spectrum of 5 mm. is the same as 1 mm. of the stronger solution containing 1/100th of a milligram-mol. From careful measurements of the spectra, the transmitted and absorbed rays, the oscillation frequencies $1/\lambda$ and the wave-lengths λ are determined for each dilution and each thickness of liquid. The curves are all obtained by straight lines joining fixed points measured on the scale of oscillation frequencies, with the exception of those portions which are represented by dotted lines indicating where the rays are more or less feebly transmitted.

The range of spectrum is from the solar line E in the green, or about $^{1}/\lambda$ 1900, to $^{1}/\lambda$ 4000 in the ultra-violet, or in wave-lengths from 5263 to 2000 tenth-metres. The curve of each substance, therefore, is strictly quantitative, and represents the internal vibrations of the molecule, as was explained in the previous communications referred to above. Although, by referring to the photographs, it is easy to understand the measurements given in detail, it is not so by mere reference to the curves. Neither the termination of the absorption band in the visible region nor the red and yellow rays which are transmitted appear on the first few photographs of isatin and its derivatives. Owing to this, in the tabulated statements of the measurements, the absorption bands are not indicated at all distinctly, although in reality they are very well defined and strong.





Methylcarbostyril. Carbostyril. Methylpseudocarbostyril. Curves of Molecular Vibrations.

$\label{eq:Carbostyril} \textit{Carbostyril}, \ C_9H_7NO.$ 0.145 gram (=1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Descri	ption of s	Spectrum.	,	¹/λ.	λ.
25	Spectrum conti				2768	3612
20	All rays beyond	l complete	ely absorb	ed.		
15	The same.	-	-			
	Spectrum conti	nuous to			2776	3602
10	All rays beyond	complete	ly absorb	ed.	-	
5	,,	,,	٠,,		2781	8595
4	, ,,	,,	,,		2786	3589
3	,,	"	33		2796	3576
2	"	,,	"		2806	8563
ī	*-	17	"		2826	3538
,	The same as (2).		,,			- 300

Carbostyril—(continued). 0·145 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/ኤ.	λ.
.4	Continuous spectrum to	2826	3588
3	showing faintly at ¹ /λ 3394. Spectrum continuous to	2856	8501 8467 to 2946
2	Spectrum continuous to	2884 2938	3467 3403 8467 to 300 9
1	Absorption band 2938—3188. Faint indication of lines at ¹ /\lambda 2949, 3064, and 3076. Spectrum continuous from 3188 to 3532. Complete absorption beyond, except strong lines at ¹ /\lambda 3686.	2938	3403 8408 to 8186

Carbostyril—(continued). 0·145 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ, 	λ.
4	Spectrum continuous to	2999	3334 8884 to 3194
3	Spectrum continuous to	3638	2748
2	Spectrum continuous to	4135	2418
1	Spectrum continuous to	4135	2418

Methylpseudocarbostyril, C₁₀H₉NO. M. p. 71°.

$$C_6H_4 < CH = CH CH N(CH_8)CO$$
.

0.159 gram (=1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.		Description	1/2.	λ.		
25	Spectrum	continuou absorption	s to	1.	2788	8652
20	Strong line showing at 1/ λ 2768.				2749	3637
15	Same as	(20).			1	
10	Complete	absorption	bevon	d	2768	3612
5	,,	,,	٠,		2768	3612
4	,,	,,	,,		2768	8612
3	,,	,,	,,		2775	3603
2	"	,,	,,	*******************	2781	3595
1	"	,,		***************************************	2791	3582

${\it Methylpseudocarbostyril} \hbox{---} (continued).$

0.159 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum,	¹/λ.	λ,
4	Spectrum continuous to	2826	3538
3	- Spectrum continuous to	2826	3538 3588 to 8004
2	Complete absorption beyond, except line at Spectrum continuous to	3886 2936	2573 3405 3405 to 8086
. 1	Complete absorption beyond, except cadmium lines at ¹ / λ 3638 and 3886. Spectrum continuous to	293 8	3408 8408 to 8188
	to 3528. Complete absorption beyond, except strong cadmium lines at 3638 and 3886.		

Methylpseudocarbostyril—(continued). 0.159 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	³/λ.	λ.
4	Absorption band 8004—8189 Lines showing at ¹ / _A 3064 and 3076.	3004	3828 8828 to 8185
	Spectrum continuous to	8898	2536
8	Spectrum continuous to	3520	2810
	Still faint between 1/\(\lambda\) 2938 and	3349	2985
2	Spectrum continuous to	4132	2420
1	Spectrum continuous to	4132	2420

Methylcarbostyril, $C_{10}H_{9}NO$. B. p. = 247°.

$C_6H_4 < N = C \cdot OCH_3$

0.159 gram (=1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Г	Description	¹/λ.	λ.		
25 20 15 10 5 4 8 2					2945 2950 2955 2965 8004 8018 8018 8038	3395 3389 3384 3372 3328 3318 3318 3818 3818

Methylcarbostyril—(continued). 0·159 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ.
4	Spectrum continuous to	8076	8250
	Lines showing between $^{1}/\lambda$ 3855 and 3638. Absorption band 8076-8410. Faint indication of spectrum from $^{1}/\lambda$		8250 to 2982
	3410 to	3520	2840
3	Spectrum continuous to	3076 -	3250 8250 to 8018
	beyond, except line at	3886	2578
2	Absorption band 8076—8185. Spectrum continuous from 1/A 8135 to 3638. Complete absorption beyond, except strong	3076	3250 8250 to 8189
1	Same as (2). Spectrum very faintly con-	3886	2573
	tinuous between 1/A 3638 and 3886; exceedingly faint continuation to about	4030	2481

Methylcarbostyril—(continued). 0·159 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	1/λ.	λ.
4	Spectrum continuous to	3886	2573
	Faint prolongation to	4080	2450
3	Spectrum continuous to	3886	2573
	Faint prolongation to	4080	2450
2	Spectrum continuous to	4135	2418
	between	4290	2381
	and	4423	2260
1	Same as (2); additional line at	4565	2190

 $Isatin, ~C_8H_8NO_2.$ 0·147 gram (=1 milligram-mol.) in 100 c.c. alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ.
25	Complete absorption of all rays beyond	1900	5268
20	The same.		
15	The same, except two strong lines appearing		1
	very feebly at	2884	8467
	and	2938	3403
10	Same as preceding, but lines more distinct.		
	Line also at	2768	3612
	Spectrum continuous, but weak, from	2884	
	1 - ' '.	2997	
_	to	2997	
5	Absorption band 1900—2768.	0840	5268 to 3612
	Line at	2768	
	Spectrum continuous, but faint, from	2826	
	to	3004	3320
	Lines $^{1}/\lambda$ 3064 and $^{1}/\lambda$ 3076 faintly transmitted.		1
4	Absorption band 1900–2768.		5263 to 3617
3	Absorption band 2088—2768.		4800 to 8612
_	Spectrum continuous 1/A 2768 to	3064	8268
2	Spectrum nearly continuous, but weak, to		3612
-	Spectrum strong 1/ λ 2768 to	8076	
	Line showing of	3638	
1	Line showing at	3638	
7	Same as (2), with lines at	9090	4/20
	and $1/\lambda$ 3886.		(3250
	Absorption band 8076—3688.		2748
	Complete absorption beyond.		(

Isatin—(continued). 0.147 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ.
4	Spectrum continuous to	3188	8186 8186 to 2748
	Faint spectrum from 1/A 3638 to	3886	2578
3	Spectrum continuous to	3240	3086 3086 to 2748
2	Faint spectrum ¹ /A 3638 to	3886	2573
	distinctly. Spectrum continuous to	3214	8111
1	Spectrum continuous to	3886 3638 3886 4 42 3	2573 2748 2578 2260

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Isatin—(continued).
0:147 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	· λ.
4	Spectrum continuous to	8900	2564
	Still somewhat faint between	3284	8045
	and	8605	2773
3	Complete absorption beyond	3900	2564
	Spectrum continuous and fairly strong to Additional lines showing at 1/\lambda 4306, 4478,	3952	2530
2	and 4828.	I	
	Spectrum continuous and strong to	3952	2530
1	Lines showing between 1/ λ 4290 and 4656. Same as (2),		

Isatin—(continued).
0.147 gram in 12,500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/ λ .	λ.
4	Spectrum continuous to	4290	2331
3	Spectrum continuous; weak between 1/\lambda 8965 and	4290	2331
2	Spectrum continuous.		ļ
1	" "		

Methylpseudoisatin, C₉H₇NO₂. M. p. 133°.

$$C_6H_4 < N(CH_8) > CO.$$

0.161 gram (= 1milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ
25 20 15	Complete absorption of all rays beyond Complete absorption beyond 1900, except lines at 1/\(\lambda\) 2884 and 2938.	1900	5263
10	Complete absorption beyond 1900, with additional line at 2768.		
5	Absorption band 1900—2768. Strong line visible at 2768.		5268 to 3612
4	All lines transmitted from 1/A 2768 to Line at 1/A 2088. Feeble, but not continuous, spectrum to 2768	3004	3328
	Absorption band feeble, 1900—2768.	3076	5268 to 3612 3250
3	All lines transmitted from 2768 to	3076 3076	3250
o o	Still somewhat feeble from 1/A 2083 to	2768	3612
2	Continuous spectrum to	3076	3250
1	Continuous spectrum to	3076	3250

Methylpseudoisatin—(continued). 0·161 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ.
4	Continuous spectrum to	3240	3086 3086 to 2748
3	A few lines showing faintly between 1/A 3240 and	3638	2748
2	Spectrum continuous to	3638 3638	2748 2748
1	Same as (2), with lines showing faintly at	4381 4425	2308 2259

Methylpseudoisatin—(continued). 0:161 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	1/λ. ·	λ.
4	Continuous spectrum to	3886	2573
	Lines showing between		2322
3	and		2206 2578
ð	Continuous spectrum to	4290	2373 2331
	and		2206
· 2	Continuous spectrum to		2552
	Lines showing between	4290	2331
	and	4656	2147
	Methylpseudoisatin—(continued 0.161 gram in 12,500 c.c. of alco	•	
Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ.

0.161 gram (= 1 milligram-mol.) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	³/A.	λ.
25	Complete absorption of all rays beyond	1900	5263
20	,, ,, ,, ,,		
15			
10	Complete absorption except line at 1/A 2083.		
5	The same as 10 with lines at 2187 and 2161.		
4	Spectrum continuous from ¹ /λ 2083 to Very faint line at 3471.	2175	4597
8	Absorption band 2175—8854. Lines showing feebly at 8354 and 8471.		4597 to 2981
2	Spectrum continuous to	2270	4405 4405 to 8608
_	Faint spectrum from ¹ /λ 2775 to	8528	2834
1 	Same as (2), but rays stronger. Very faint line at	8644	274400

Methylisatin—(continued). 0.161 gram in 500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	³/λ.	λ.
4	Continuous spectrum to	2357	4242
•	Very faint indication of lines from 2443 to Absorption band 2472—2768.	2472	4045 4045 to 8612
	Rather weak spectrum from 1/\(\lambda\) 2768 to Complete absorption beyond.	3638	2748
8	Continuous spectrum to	2502	8996 8996 to 8612
	Spectrum from 1/\(\lambda\) 2768 to	3638	2748
2	Same Absorption band but feebler from 2502—2768.		8996 to 8612
1	Same as preceding; line at	3886	2578

Methylisatin—(continued). 0.161 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ.
4	Continuous spectrum to	3688 3783	2748 2678
3	Continuous spectrum to	8688 3900	2748 2564
2	Spectrum continuous to	4088	
1	Continuous spectrum to	4120	2427

Methylisatin—(continued). 0.161 gram in 12,500 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of Spectrum.	¹/λ.	λ.
4	Continuous spectrum to	4185 8886 4185	2418 2578 2418
3	Continuous spectrum.		
2	,, ,,		
1	" "		,
			godle

Our best thanks are due to Mr. Alexander Lauder, of the University College of North Wales, Bangor, for his assistance in the general work of the research, and especially for the great care he has taken in preparing the substances examined.

We are now engaged in a more comprehensive research on this subject, embracing the examination of the absorption spectra of derivatives of etheric succinosuccinates, phloroglucinol, and other substances which exhibit tautomeric phenomena.

The various expenses of this investigation were partly defrayed by a grant from the Government Grant Fund of the Royal Society.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

LXIII.—Preparation of Acid Phenylic Salts of Dibasic Acids.

By SAMUEL BARNETT SCHRYVER, D.Sc., Ph.D.

It has long been known that anhydrides of dibasic organic acids, on treatment with alcohols or with alcoholic solutions of sodium alcoholates, are readily converted into the acid alkylic salts or their corresponding sodium compounds. Under certain conditions, which will be specified, sodium derivatives of phenols are capable of forming sodium phenylic salts by interaction with the anhydrides of dibasic organic acids, in accordance with the general equation:

$$XONa + R < \frac{CO}{COOX} = R < \frac{COONa}{COOX},$$

where X is the phenylic residue, and R the residue of a dibasic acid (compare Walker, Trans., 1892, 41, 1089). The reaction must be carried out in the presence of a liquid which is incapable of acting chemically either on the sodium salt or the anhydride, and xylene was employed in most cases, as it can be heated on a water-bath without the necessity of using a condenser; several other hydrocarbons are, however, equally suitable.

The sodium salt is very conveniently prepared in most cases by the direct action of sodium on a solution of the phenol in the solvent in which the reaction is to be carried out. The reaction generally takes place immediately on adding the anhydride to the sodium salt, and often with the evolution of a considerable amount of heat; on cooling, the sodium phenylic salt separates, generally in a gelatinous form, and can be extracted with water. From the aqueous solution thus obtained, the acid salt can be precipitated by the addition of mineral acids.

The reaction is also applicable to substituted phenols, but of these there are two classes at present known, which will not react with anhydrides in the way just described.

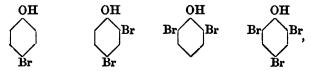
(a) The Ortho- and Para-nitrophenols.—Whereas metanitrophenol acts on camphoric anhydride with ease, the ortho- and para-derivatives do not react with it, even when the mixture is heated to 180°.

Several instances have been pointed out recently in which the meta-compound acts quite differently from both the ortho- and paraderivatives. Lobry de Bruyn (Rec. Trav. Chem., 1894, 13, 101) has shown that whereas ortho- and para-dinitrobenzene are readily converted into ethoxynitrobenzenes by the action of alcohol, the meta-compound does not react with alcoholic ammonia, even at 250°. Menschutkin (Ber., 1897, 30, 2968) shows further that meta-nitrobromobenzene will not react with dipropylamine, although both the ortho- and para-derivatives form condensation products with it with relative ease. On the other hand, metatoluidine acts on allylic bromide more readily than either the ortho- or para-compound, the relative rates of reaction being 54 for the ortho-, 445 for the meta-, and 96 for the para-derivative.

It will be noted that in the two cases where a metanitro-compound does not react, the strongly negative nitro-group causes the other substituted group or element to resist the action of a basic substance (alcoholic ammonia or propylamine). The converse is observed, however, in the action of nitrophenols on anhydrides, and whilst the nitro-group protects the hydroxyl radicle in the ortho- or paraposition, metanitrophenol readily reacts with a substance of acidic character.

(b) The Diortho-substituted Phenols.—V. Meyer and his pupils have shown that substituted benzoic acids, with the two substituent groups in the ortho-position relatively to the carboxylic group, are incapable of forming alkyl salts when treated with an alcohol and hydrochloric acid (V. Meyer and Sudborough, Ber., 1894, 27, 510, 512, 1580, 3146); benzamides derived from such acids, moreover, appear to be hydrolysed with very great difficulty (Sudborough, Trans., 1895, 65, 603). The sodium salts of diortho-substituted phenols will not condense with anhydrides.

This law has been confirmed by an investigation of the reactions of the following bromophenols with camphoric anhydride:



as it was observed that, whereas the sodium salt of the first two compounds readily underwent condensation, yielding the well crystallised bromophenyl hydrogen camphorates on acidification, the other two bromophenols did not react even at 180°.

The analogy between these facts and those observed by V. Meyer and his pupils on the etherification of substituted benzoic acids is certainly striking. The general law, however, has only been tested by the reactions of the bromo-substitution products, as pressure of other work has prevented me from following this subject further. It must therefore be left an open question whether the non-reactivity of the diortho-substituted products is to be ascribed to the stereochemical influence of the substituent groups (V. Meyer), or to the proximity of the hydroxyl radicle to two other groups of strongly negative character; in other words, whether it is due to a dynamic or a static cause.

In the action of camphoric anhydride on sodium derivatives of phenols, only one acid phenylic salt was obtained in each case, except in that of metanitrophenyl camphorate, which was formed in very small quantity; the crystalline compounds seemed homogeneous, and melted sharply, frequent recrystallisation failing to alter the melting point to any appreciable extent. No mixtures corresponding to the allo- or ortho-monomethylic salts were obtained (Braunschweig, Ber., 1892, 25, 1806; Walker, Trans., 1892, 41, 1089).

Several of the products described in the following work may find applications for therapeutic purposes.

EXPERIMENTAL.

I. Action of Anhydrides on the Sodium Derivatives of simple Phenols, or Ethers of polyhydric Phenols.

Phenyl Hydrogen Camphorate, COOH·C₈H₁₄·COO·C₆H₅.—Sodium, in wire or small pieces, was added to a molecular proportion of pure phenol dissolved in ten times its weight of xylene, and the mixture warmed to about 90°; the sodium dissolved, and the sodium phenate which is formed separated as a white powder. As soon as this action was completed, a molecular equivalent of camphoric anhydride was added to the solution while still warm, and the mixture vigorously shaken; the sodium phenate dissolved almost immediately, and after a short time sodium phenyl camphorate separated in a gelatinous form. The mixture was vigorously shaken with water, equal in volume to that of the xylene, to dissolve the sodium salt, and on acidifying, phenyl hydrogen camphorate separated as an oil. This was taken up with ether, the ethereal solution dried over calcium chloride, and after distilling off the ether, the residue was left in a vacuum for a few days, when the light yellow oil commenced to solidify, forming hard

clusters of radiating needles, which can be separated only with some difficulty from the sides of the crystallising basin. After drying on a porous plate and recrystallising from a mixture of chloroform and light petroleum, they melted sharply at 100°.

0.1086 gave 0.2768 CO₂ and 0.0709 H₂O. C = 69.51; H = 7.25. $C_{16}H_{20}O_4$ requires C = 69.56; H = 7.25 per cent.

Thymyl Hydrogen Succinate, COOH·CH₂·CH₂·COO·C₁₀H₁₃.—Thymol dissolved in xylene was treated with metallic sodium, the same relative quantities being used as in the preparation of sodium phenate. The sodium derivative of thymol is readily soluble in xylene, and since the solution darkens very rapidly—as a result, probably, of oxidation—the anhydride should be added as soon as the sodium has dissolved; the dark colour of the solution then disappears, and the sodium thymyl succinate separates in the form of a light yellow, gelatinous mass. It is extracted with water, and the acid salt, precipitated from the aqueous solution, separates as an oil which very readily solidifies, forming a mass of granular crystals. For analysis, it was twice recrystallised from a mixture of chloroform and light petroleum, from which it separated in aggregates of well-defined crystals melting at 121—122°.

0.1145 gave 0.2809 CO_2 and 0.0780 H_2O . C = 66.89; H = 7.56. $C_{14}H_{18}O_4$ requires C = 67.20; H = 7.20 per cent.

Thymyl Hydrogen Phthalate, COOH·C₆H₄·COO·C₁₀H₁₃.—This compound, prepared in exactly the same way as the corresponding succinate, is precipitated from the solution of the sodium salt as an oil which readily solidifies; it forms aggregates of well-defined crystals when precipitated from an ethereal solution by light petroleum, and the specimen analysed was twice recrystallised in this way.

0.1267 gave 0.3371 CO₂ and 0.0669 H₂O. C = 72.55; H = 5.82. $C_{18}H_{18}O_4$ requires C = 72.47; H = 6.04 per cent.

Thymyl Hydrogen Camphorate, COOH· C_8H_{14} ·COO· $C_{10}H_{13}$.—This salt, prepared by a similar method from camphoric anhydride, is precipitated by mineral acids from the solution of its sodium salt as an oil which often does not solidify for several days; it then forms an indistinct, light yellow mass, which is readily soluble in ether, chloroform, and light petroleum. The specimen analysed was twice recrystallised from the last named solvent, from which it separated in the form of hard, nodular masses melting at 89°. It has a slight local anæsthetic action, producing a feeling of numbness when placed on the back of the tongue.

0.1172 gave 0.3119 CO_2 and 0.900 H_2O . C = 72.58; H = 8.52. $C_{20}H_{28}O_4$ requires C = 72.28; H = 8.43 per cent.

The sodium salt of this compound, like the other sodium thymyl salts, is very readily hydrolysed by warm water; the acid salts, on the other hand, are fairly stable.

Guaiacyl Hydrogen Camphorate, COOH·C₈H₁₄·COO·C₆H₄·OCH₈.— Guaiacol, dissolved in ten times its weight of xylene, is heated at about 90° with a molecular proportion of sodium, either in wire or small slices; the sodium derivative thus formed is fairly readily soluble in warm, although sparingly so in cold xylene. As soon as the sodium has dissolved, camphoric anhydride (1 mol.) is added to the solution while still warm, and an immediate reaction takes place, sodium guaiacyl camphorate separating after a short time as a white, somewhat gelatinous This is extracted with water, and, on acidifying, guaiacyl hydrogen camphorate separates as an oil, which begins to crystallise almost immediately and after a short time forms a hard, granular mass which can be readily pounded in a mortar. The camphorate analysed was twice recrystallised from a mixture of chloroform and light petroleum, from which it separated in white, glistening needles melting at 112°. It is very soluble in acetone or alcohol, the concentrated solution in the latter forming a thick syrup.

0.1018 gave 0.2476 CO₂ and 0.0675 H₂O. C = 66.33; H = 7.46. $C_{17}H_{22}O_5$ requires C = 66.61; H = 7.13 per cent.

4.2064 substance dissolved in alcohol required for complete neutralisation 13.9 c.c. (calculated 13.5 c.c.) of N-soda, with phenolphthalein as indicator. The neutral solution thus prepared, after dilution with water, gave the following reactions:

AgNO₈. White precipitate, rapidly darkening.

HgCl₂. White, gelatinous precipitate.

FeCl_s. Buff-coloured precipitate, rapidly turning grey.

CuSO₄. Bright green precipitate.

ZnCl₂. White precipitate.

Bi(NO₃)₃. White precipitate.

Normal guaiacyl camphorate, $C_8H_{14}(COO \cdot C_6H_8 \cdot OCH_8)_2$, was prepared by warming the acid salt with a molecular equivalent of phosphorus pentachloride, adding a molecular equivalent of guaiacol, and heating on the water-bath until only small quantities of hydrogen chloride were evolved; the product was then poured into ice-water. The normal salt, which at first separated as an oil, but solidified after a short time, was then recrystallised once or twice from hot alcohol, in which it is readily soluble, although only sparingly so in the cold. The specimen analysed was crystallised finally from a mixture of chloroform and light petroleum, and was obtained in stellate clusters of thin, white needles which melted at 124°,

0.1231 gave 0.3162 CO₂ and 0.0800 H₂O. C=70.05; H=6.58. $C_{24}H_{23}O_{5}$ requires C=69.90; H=6.79 per cent.

Guaiacyl Hydrogen Succinate, COOH·CH₂·CH₂·COO·C₆H₄·OCH₈.— Owing to the readiness with which the sodium salt undergoes hydrolysis, the following method was adopted for its preparation; benzene was used instead of xylene, and the sodium guaiacyl succinate was collected, pressed, dried, powdered, and thrown in small quantities at a time into 10 per cent. sulphuric acid on which a layer of ether The acid salt thus formed was immediately taken up by the ether, and remained only for a very short time in contact with the water. After evaporating the ether and leaving the residue in a vacuum for some days, a mass of crystals was obtained, which was dried on a porous plate and then dissolved in ether: the ethereal solution, after filtration from a small quantity of sparingly soluble matter, was mixed with sufficient light petroleum to precipitate only a portion of the substance, as the first fraction was likely to contain small quantities of succinic acid. The crystalline residue, obtained by evaporating the filtrate, was dissolved in chloroform, to which light petroleum was then added, the succinate separating in beautiful, stellate aggregates of needles which melted at 75°.

0.1070 gave 0.2301 CO_2 and 0.0504 H_2O . C = 58.65; H = 5.23. $C_{11}H_{12}O_5$ requires C = 58.93; H = 5.35 per cent.

Carvacryl Hydrogen Camphorate.—Sodium dissolves in a warm solution of carvacrol in xylene, and the sodium derivative crystallises on cooling. Carvacrol hydrogen camphorate prepared in the usual way forms a syrup, which does not crystallise even when surrounded by a cooling mixture.

Rugenyl Hydrogen Camphorate, COOH·C₈H₁₄·COO·C₉H₈·OCH₃.—Sodium dissolves readily in a mixture of a hydrocarbon and eugenol, forming a dark coloured solution. The eugenyl hydrogen camphorate, when isolated in the ordinary way, is a dark coloured mass which can be purified by boiling its solution in benzene with animal charcoal, and finally recrystallising from benzene and light petroleum. It melts at 115·5°.

0.4856 gram was equivalent to 13.9 c.c. N/10 sulphuric acid (calculated 14.0 c.c.) when titrated in alcoholic solution with barium hydroxide, using phenolphthalein as indicator.

 β -Naphthyl Hydrogen Camphorate, COOH·C₈H₁₄·COO·C₁₀H₇.— Sodium dissolves with some difficulty in a solution of β -naphthol in xylene, and the sodium salt thus formed has a somewhat dark colour. It reacts readily, however, with camphoric anhydride, and the β -naphthyl hydrogen camphorate can be isolated easily, but is obtained pure

only with difficulty, as it is somewhat strongly coloured when first precipitated. In order to recrystallise it, light petroleum is added to its solution in chloroform until a permanent turbidity is produced; more light petroleum is then poured carefully over this mixture, so as to form a layer on the top and as it slowly diffuses through the heavier underlying liquid, the naphthyl camphorate separates in radiating clumps of light pink crystals which melt at 121—122°.

0.4644 gram corresponds to 14.1 N/10 sulphuric acid (calculated 14.0 c.c.) when neutralised with barium hydroxide in alcoholic solution, using phenolphthalein as indicator.

II. Action of Anhydrides on Substituted Phenols.

In the reactions described under this heading, camphoric anhydride was used, for the following reasons:

- (a) Its solubility in xylene, in which all the reactions were carried out: hence the greater ease with which it reacts, compared with other anhydrides.
- (b) The relatively greater stability of the camphorates as compared with the succinates and other acid salts investigated: hence the greater ease in isolating the products of reaction.

Salyl Hydrogen Camphorate.—Sodium dissolves in a warm solution of salol (phenyl salicylate) in xylene, forming a white derivative which readily reacts with camphoric anhydride; the product is a thick syrup which does not crystallise on long standing, even when surrounded by a freezing mixture.

Nitrophenols and Camphoric Anhydrids.—The sodium orthonitrophenate for these experiments was made, partly by the direct action of sodium on a warm solution of the phenol in xylene and partly by dissolving the phenol in alcohol, adding the theoretical quantity of sodium ethoxide in alcohol, and precipitating the red sodium salt thus formed by ether. The sodium derivative of the paranitrophenol was prepared by the former, that of the meta-derivative by the latter method. Neither the ortho- nor the para-derivative reacted with camphoric anhydride, even after prolonged heating at 180°; the metanitro-compound, however, entered into reaction with it fairly readily.

Metanitrophenyl hydrogen camphorate, COOH·C₈H₁₄·COO·C₆H₄·NO₂.

—This salt was obtained when camphoric anhydride was dissolved in ten times its weight of xylene, the solution heated on a water-bath, and the solid metanitrophenol added, with continual stirring; after a time, the red compound dissolved, and, on cooling, the nitrophenyl camphorate separated in the form of a light yellow, gelatinous mass. The acid camphorate, isolated in the usual way, completely solidified after some time. It was insoluble in light petroleum and only

slightly soluble in chloroform, but dissolved readily in warm benzene, from which it was precipitated by light petroleum. It commenced to melt at 115°, although it was not completely fused until some degrees higher. Possibly the substance was a mixture of the allo- and orthocompounds.

0.2243 gave 8.6 c.c. moist nitrogen at 15° and 767 mm. N = 4.4. $C_{16}H_{19}NO_6$ requires N = 4.3 per cent.

Succinic anhydride heated with the sodium derivative of orthonitrophenol also gave no reaction. Probably the method just described may be generally applied to nitrophenols to distinguish the metafrom the ortho- and para-compounds.

Action of Camphoric Anhydride on Sodium Bromophenates.

Parabromophenyl Hydrogen Camphorate, COOH· C_8H_{14} ·COO· C_6H_4 Br.—Sodium readily dissolves in a warm solution of parabromophenol in xylene, forming a white derivative; this goes into solution on adding camphoric anhydride, and the mixture deposits sodium bromophenyl camphorate on standing. On acidifying the aqueous solution of this salt with mineral acids, the acid separates almost immediately in a crystalline form. It is very readily soluble in chloroform, and when precipitated from solution in this solvent by light petroleum, separates in radiating masses of hard, thick needles, which are not perfectly white and melt at 111° .

0.2421 gave 0.1303 AgBr. Br = 22.9. $C_{16}H_{19}BrO_4$ requires Br = 22.6 per cent.

2:4-Dibromophenyl Hydrogen Camphorate, COOH·C₈H₁₄·COO·C₆H₈Br₉.

—2:4-Dibromophenol was prepared by the action of bromine on a solution of phenol in carbon bisulphide in the presence of small quantities of aluminium chloride. The carbon bisulphide solution of the bromophenol thus formed was washed, first with water, then with dilute alkali, and dried; after removing the carbon bisulphide by evaporation, the residue was fractionally distilled in a vacuum.

From the pure dibromo-compound thus obtained, 2: 4-dibromophenyl hydrogen camphorate was prepared in exactly the same way as the corresponding monobromo-derivative. It very readily crystallises, and is easily soluble in hot, although somewhat sparingly in cold, chloroform, and separates in the form of dendritic masses of small crystals melting at 173°.

0.1711 gave 0.1467 AgBr. Br = 36.5. $C_{16}H_{18}Br_{2}O_{4}$ requires Br = 36.8 per cent, Action of Camphoric Anhydride on Sodium 2:6-Dibromophenate.

2:6-Dibromophenol was obtained in small quantity by distilling tetrabromophenolphthalein with concentrated sulphuric acid (Baeyer, Annalen, 1880, 202, 138); the yield, however, was extremely small. It was finally prepared from Fischer and Hepp's diorthobromamidophenol (Ber., 1888, 21, 674).

This was dissolved in four times its weight of alcohol, and to the solution rather more than the theoretical quantity of ethylic nitrite was added in 16 per cent. alcoholic solution; after some time, the whole was dropped gradually into an equal bulk of boiling alcohol, and kept in the state of constant ebullition for about one hour. The alcohol was then distilled off, and the residual oil distilled in steam. The dibromophenol thus obtained, being somewhat coloured, was purified by fractional distillation in a vacuum, and then had a constant boiling point not far removed from that of the 2:4-dibromo-compound.

2:6-Dibromophenol did not react with camphoric anhydride, either when treated under the same conditions as the 2:4-bromo-compound, or when the mixture was heated in sealed tubes at 150°.

The 2:4:6-tribromophenol was prepared in the usual way, and recrystallised several times from aqueous alcohol. It reacted with the anhydride neither at the temperature of a water-bath nor at 180° in sealed tubes.

Action of Camphoric Anhydride on Sodium Nitrosophenates.

Sodium derivatives were made from nitrosophenol and nitrosothymol by the action of sodium ethoxide on the alcoholic solutions and precipitation by ether. The sodium derivative of nitrosothymol prepared in this way did not separate immediately but only after some little time; it crystallised in dichroic golden plates reflecting a green light, and when dried in mass formed a brick-red powder.

When warmed with a 10 per cent. solution of camphoric anhydride in xylene on a water-bath, the sodium derivative of nitrosophenol charred before any reaction occurred. A similar result was obtained with nitrosothymol, although the latter, when left for a long time with a more dilute solution of the anhydride in xylene, partially disappeared, forming a white sodium salt which was not further investigated.

THE WELLOOME CHEMICAL RESEARCH LABORATORIES.

LXIV.—Corydaline. Part VI.

By James J. Dobbie, D.Sc., M.A., and Alexander Lauder.

In a former paper (Trans., 1895, 67, 17), we gave an account of the separation from the products of oxidation of corydaline with potassium permanganate of a compound having the composition $C_9H_7NO(OCH_8)_2$, which we provisionally named corydaldine. By altering the conditions of oxidation, we have obtained a larger yield of this substance, and have examined its reactions and decomposition products more fully. In the paper referred to, we gave analyses of corydaldine together with the results of the determination of the methoxy-groups, and we showed that this substance has a neutral reaction in aqueous solution, and that it does not combine, at all events readily, with phenylhydrazine.

Freund and Josephi (Annalen, 1893, 277, 10), from the similarity in behaviour of methylcorydaline and hydrohydrastinine, and especially from the stability of their alkylic haloid addition compounds towards alkali, infer that corydaline, like hydrastine, contains a methyl group attached to the nitrogen atom. J. Herzig and H. Meyer (Monatsh., 1897, 18, 385), on the other hand, found that corydaline only contains four methyl groups in all, which can be split off by the action of hydrogen iodide, and we had previously shown that it contains four methoxy-groups. It follows, therefore, that methyl is not attached to the nitrogen atom in this alkaloid. We have arrived at the same conclusion by an entirely different method. By acting on corydaldine with nitrous acid, we obtained a highly characteristic nitrosoderivative, C₁₁H₁₂N₂O₄. When gently warmed with a dilute solution of sodium hydrate, this substance goes into solution, evolving nitrogen and forming a sodium salt, C1, H1, O5Na, which, on treatment with hydrochloric acid, yields the anhydride of the acid C₁₁H₁₄O₅. The anhydride C₁₁H₁₂O₄ contains two methoxy-groups. On oxidation with potassium permanganate, it yields metahemipinic acid, and when heated under pressure with dilute hydrochloric acid, it gives a phenolic compound which we believe to be identical with \(\omega\)-hydroxyethylcatecholcarboxylic anhydride, obtained by Perkin from berberine (Trans., 1890, 57, 1027).

Corydaldine is therefore closely allied to Perkin's ω -amidoethyl-piperonylearboxylic anhydride, from which it differs only in containing two methoxy-groups in place of the piperonyl or $CH_2 < 0$. group. Like Perkin's substance, it is a secondary base, and the derivatives of the one bear a very close resemblance to the correspond-

ing derivatives of the other, the relation between the two series of compounds being shown by the following formulæ:—

$$\begin{array}{c} \operatorname{CH_3O} \\ \operatorname{CH_3O} \\ \operatorname{C_6H_2} \\ \operatorname{CO-NH} \\ \operatorname{CH_2} \\ \operatorname{CH$$

Corydaline is thus brought into close relation, not only with berberine, but also with hydrastine, narcotine, and papaverine, in common with which it contains an isoquinoline nucleus. From oxyhydrastinine, corydaldine only differs in containing two methoxygroups in place of the piperonyl group, and in having a hydrogen atom in place of a methyl group united with the nitrogen atom. That the arrangement of the groups attached to the benzene nucleus is the same in both substances, is confirmed by the oxidation on the one hand of the anhydride $C_{11}H_{12}O_4$ to metahemipinic acid, and on the other hand by the conversion of hydrastic acid into 4:5-dihydroxyphthalic acid (normetahemipinic acid) by the action of phosphorus pentachloride and water.

Prof. W. H. Perkin has recently suggested to us that it might be possible to convert ω-amidoethylpiperonylcarboxylic anhydride into corydaldine, by first preparing its phenolic derivative and then methylating, and he has very kindly furnished us with a quantity of the anhydride for the purpose of making the experiment.

In the paper already referred to, we gave an account of the separation of hemipinic acid $[(COOH)_3:(OCH_3)_2=1:2:3:4]$, from the products of oxidation of corydaline with potassium permanganate, and stated fully our reasons for considering the acid so obtained to be identical with the hemipinic acid from narcotine and berberine. In a later paper (Dobbie and Marsden, Trans., 1897, 71, 657), it was

stated that metahemipinic acid $[(COOH)_2:(OCH_3)_2=1:2:4:5]$, identical with the hemipinic acid from papaverine, had also been obtained amongst the products of oxidation of corydic acid, $C_{18}H_{17}NO_6$, with potassium permanganate. We have now succeeded in separating metahemipinic acid, as well as hemipinic acid, from the products of the direct oxidation of corydaline with potassium permanganate.

The formation of metahemipinic acid by the oxidation of the anhydride, $C_{11}H_{12}O_4$, obtained from corydaldine shows that this acid is derived from the benzene ring of the isoquinoline nucleus. We thus obtain an important clue to the constitution of corydic acid which must also contain the isoquinoline nucleus, since it likewise yields metahemipinic acid on oxidation. It follows, therefore, that the ring which is destroyed when corydaline is oxidised with dilute nitric acid is the ring which yields hemipinic acid when the alkaloid is oxidised with potassium permanganate.

It is thus established that corydaline contains an isoquinoline nucleus and a benzene ring, to each of which two methoxy-groups are attached. We have therefore accounted satisfactorily for 19 of the 22 carbon atoms of the alkaloid.

In a former paper (Trans., 1894, 65, 57), we described one of the products of the oxidation of corydaline with a boiling solution of potassium permanganate, under the name of corydalinic acid. Had our original view of the nature of this substance been correct, a nitrogenous acid should have been found amongst its products of oxidation. As every attempt to obtain such an acid failed, we have made a complete reinvestigation of this substance, and find that it is, in reality, a sparingly soluble ammonium hydrogen metahemipinate, $C_{10}H_{10}O_6C_{10}H_9O_6\cdot NH_4 + 3H_9O$; the analyses of the substance agree perfectly with this formula, and those of its supposed salts with the formulæ of the corresponding metahemipinates. The error arose through the earlier oxidations with permanganate having been effected without the addition of alkali, preliminary experiments having led us to believe that the potassium of the permanganate was more than sufficient for the neutralisation of all the acid produced. In the absence of any reason for suspecting the presence of ammonia, the analyses of the supposed acid and its derivatives naturally led to the formula which we assigned to it; the sparing solubility of the substance in water and the strong acid reaction of its solution, moreover, seemed to confirm the belief that we were dealing with an acid. The discovery of the error has removed the inconsistencies which appeared to exist between the results obtained by oxidising corydaline with potassium permanganate and nitric acid respectively.

EXPERIMENTAL.

After numerous experiments had been made with the view of ascertaining the most favourable conditions for the preparation of this substance, the following method was found to give the most satisfactory results: 10 grams of finely powdered corydaline were suspended in about 1 litre of water, and 18 grams of potassium permanganate dissolved in about half a litre of water were gradually added in small quantities at a time. The operation was conducted at the ordinary temperature, and required about 48 hours for completion. The precipitated manganese oxide, which was mixed with a considerable quantity of a colourless, crystalline substance, was removed by filtration, and the solution concentrated by evaporation. During concentration, a quantity of yellow, crystalline matter separated out. After filtration, the liquid was repeatedly extracted with chloroform until this was no longer coloured; the chloroform was then evaporated in a current of air at the ordinary temperature, and the residue, which was gummy in character, was thoroughly extracted with cold water. The aqueous extract, on concentration, yielded a crop of large, well-developed, prismatic crystals of corydaldine. By this method, the yield of corydaldine was 4-5 grams from 100 grams of corydaline. The substance obtained in this way melts at 175°; it is very easily soluble in chloroform, easily soluble in water, alcohol, ether, benzene, and acetic acid, but is insoluble in light petroleum. The analysis of corydaldine has already been given (Trans., 1895, 67, 20).

The nitroso-derivative was easily obtained by the following method: 3 grams of the finely powdered corydaldine were dissolved in 100 c.c. of hydrochloric acid of sp. gr. 1·1 by gently warming on the waterbath. The solution, after being diluted by the addition of 75 c.c. of water, was cooled to 0° in a freezing mixture of ice and salt, and 15 c.c. of a 10 per cent. solution of sodium nitrite were added drop by drop, the temperature being kept at 0° during the reaction. After a short time, the nitroso-derivative separated in yellow flocks. It was collected by the aid of a pump, well washed with water, and purified by crystallisation from alcohol.

The nitroso-derivative is a yellow, crystalline substance which melts at 185°. It is easily soluble in hot alcohol, from which it crystallises

in beautiful, yellow needles; it is also easily soluble in cold chloroform, and soluble in benzene or carbon bisulphide, but only sparingly so in boiling water or in ether, and insoluble in light petroleum. The nitroso-derivative is insoluble in cold alkali, but is decomposed on gently heating, with evolution of nitrogen. When treated with phenol and sulphuric acid, it gives Liebermann's nitroso-reaction, the red colour which is at first produced changing to a beautiful blue on the addition of excess of dilute alkali.

On analysis, the pure substance, dried at 100°, gave the following results:—

I. 0.2417 gave 0.5002 CO₂ and 0.1122 H₂O. C = 56.44; H = 5.15. II. 0.2687 ,, 0.5547 CO₂ ,, 0.1271 H₂O. C = 56.30; H = 5.25. III. 0.2372 ,, 23.2 c.c. nitrogen at 12° and 761.5 mm. N = 11.78. C₁₁H₁₂N₂O₄ requires C = 55.93; H = 5.08; N = 11.86 per cent.

Preparation and Properties of the Anhydride,
$$\begin{array}{c}
\mathrm{CH_3O} \\
\mathrm{CH_3O}
\end{array}
\xrightarrow{\mathrm{CO}}
\begin{array}{c}
\mathrm{CO} \\
\mathrm{CH_2}
\end{array}
\xrightarrow{\mathrm{CO}}
\xrightarrow{\mathrm{CH_2}}$$

When the nitroso-derivative is heated on the water-bath with a dilute solution of caustic soda, it goes into solution, nitrogen being evolved. The reaction that occurs may be represented as follows:

$$\frac{\text{CH}_3\text{O}}{\text{CH}_3\text{O}}\!\!>\!\!\text{C}_6\text{H}_2\!\!<\!\!\frac{\text{CO}\!-\!\text{N}\!\cdot\!\text{NO}}{\text{CH}_2}\!+\!\frac{\text{Na}}{\text{OH}}\!=\!\frac{\text{CH}_3\text{O}}{\text{CH}_3\text{O}}\!\!>\!\!\text{C}_6\text{H}_2\!\!<\!\!\frac{\text{CO}\!-\!\text{ONa}}{\text{CH}_2\!\cdot\!\text{CH}_2\!\cdot\!\text{OH}}\!+\!\text{N}_2\!\cdot\!$$

On acidifying the filtered solution with hydrochloric acid, and leaving it for some time, beautiful clusters of long, thin, flat, prismatic crystals separate out which are readily purified by recrystallisation from water. The anhydride melts at 138—139°, dissolves sparingly in cold, but readily in boiling water, and is also soluble in alcohol, ether, benzene, or acetic acid, very soluble in chloroform, but insoluble in cold light petroleum. It does not contain nitrogen. The pure substance, after drying at 100°, gave the following results on analysis:

I. 0.2208 gave 0.5103 CO_2 and 0.1163 H_2O . C = 63.03; H = 5.85. II. 0.2330 ,, 0.5422 CO_2 ,, 0.1230 H_2O . C = 63.46; H = 5.86. $C_{11}H_{12}O_4$ requires C = 63.46; H = 5.77 per cent.

Determination of methoxy-groups:

0.2173 gave 0.4834 AgI. $OCH_3 = 29.38$. $C_9H_6O_2(OCH_3)_2$ requires $OCH_3 = 29.80$ per cent.

Titration of the Anhydride with Potassium Hydroxide.—In order to determine the basicity of the acid $C_{11}H_{14}O_5$, corresponding to the anhydride $C_{11}H_{12}O_4$, the latter was dissolved in excess of a standard

solution of potassium hydroxide, and the excess of alkali determined by titration with a standard solution of sulphuric acid, phenolphthalein being used as indicator.

0.3978 gram required 30.75 c.c. KOH solution containing 0.00359 gram KOH in 1 c.c. = 0.1103 gram KOH. This proves that the acid is monobasic, for on this assumption it would require 0.1074 gram KOH.

When the neutral solution is acidified with hydrochloric acid, the anhydride separates instead of the acid, and we have not yet succeeded in obtaining the latter.

Action of Hydrochloric Acid on the Anhydride.—As we found it impossible to separate the phenolic substance corresponding to the anhydride C11H100 from the residue obtained by heating the anhydride with hydriodic acid, we endeavoured to obtain it by heating with hydrochloric acid under pressure. In each experiment, 0.5 gram of the finely powdered anhydride, 5 c.c. of hydrochloric acid of sp. gr. 1.168, and 20 c.c. of water were used, and the mixture was first heated in a sealed tube for 5 hours at 170-175°, the temperature which Perkin found most advantageous for the preparation of w-hydroxyethylcatecholcarboxylic anhydride from w-hydroxyethylpiperonylcarboxylic anhydride. Under these conditions, the anhydride was almost completely decomposed, a considerable quantity of carbon separating out, and scarcely any crystalline matter could be extracted with ether from the liquid. At 140°, very little, if any, change took place. The best result was obtained at 147-153°. If a higher temperature than this was employed, a separation of carbon invariably occurred, whilst at lower temperatures a large proportion of the anhydride was not altered. The limits of temperature, therefore, within which the reaction takes place are very narrow, as Perkin found in the case of the corresponding derivative from berberine, and a large quantity of material was used up in determining them. The contents of two tubes which had been heated to 147-153° were thoroughly extracted with ether, the ethereal solution dried over calcium chloride, and evaporated to dryness at the ordinary temperature under diminished pressure. The almost colourless, crystalline deposit which remained had not a sharp melting point; the crystals, therefore, were very gently warmed with successive small quantities of water, the aqueous solution evaporated to dryness at the ordinary temperature, and the residue dissolved in alcohol. When the alcoholic solution was evaporated at the ordinary temperature, small, thin crystals of the phenolic compound melting at 232° were obtained. The portion less soluble in water melted a little below the correct melting point of the anhydride C11H12O4. We found that the separation of the phenolic compound from the anhydride could also

be effected by means of chloroform, in which the anhydride is much the more soluble.

The crystals of the phenolic compound obtained from the alcoholic solution dissolve in a solution of potassium hydrate, forming a yellow coloured liquid. In aqueous solution, they give a deep green colour with ferric chloride, and immediately reduce both an ammoniacal solution of silver nitrate and Fehling's solution in the cold; they also give a white, amorphous precipitate with lead acetate, which dissolves in hot water. The phenolic derivative is more soluble in water than the anhydride, and is soluble in ethylic alcohol, but only sparingly so in chloroform. This substance gives, therefore, all the reactions of ω -hydroxyethylcatecholcarboxylic anhydride as described by Perkin; the melting point, however, is a few degrees higher. Our stock of the anhydride $C_{11}H_{12}O_4$ having been exhausted in determining the conditions under which its phenolic derivative is formed, we are unable at present to give analyses of this substance.

Oxidation of the Anhydride C11H12O4 with Potassium Permanganate.

One gram of the anhydride was dissolved in hot water, and a dilute solution of potassium permanganate added until it was no longer decolorised, the oxidation being effected at the boiling point. After filtration from the manganese oxide and concentration, the solution was precipitated with lead acetate, and the precipitate, which was almost white in colour, washed with water and decomposed with sulphuretted hydrogen. The filtrate from the lead sulphide yielded, on evaporation, colourless, prismatic crystals, which, after recrystallisation, were found to melt at the same temperature as metahemipinic acid when the two substances were tested side by side. The acid and the ethylimide prepared from it gave all the tests for metahemipinic acid which are detailed in a later part of the paper.

Hemipinic Acids from Corydaline.

In an earlier paper (Trans., 1894, 65, 57), we mentioned that, after the removal of the readily crystallisable matter from the products of oxidation of corydaline with potassium permanganate at the boiling point, there remained a clear yellow, gummy mass with a strong acid reaction. After removal of some tarry matter by repeated solution, evaporation, and filtration, we obtained from this mass:

- (1) A small quantity of slender, yellow, silky needles which were sparingly soluble in water, and melted at 221—222°.
- (2) A large quantity of colourless crystals, which proved to be separable into two portions, differing considerably in their solubility

in water, a complete separation of the two substances being effected by fractional crystallisation.

The more soluble fraction was found to be identical with the hemipinic acid already described as occurring amongst the products of oxidation with potassium permanganate (Trans., 1895, 67, 18). To confirm this conclusion, a portion was converted into the ethylimide (loc. cit.) which melted at 92°, and, after drying over concentrated sulphuric acid, gave the following numbers on analysis:

0.2255 gave 0.5062
$$CO_2$$
 and 0.1152 H_2O . $C = 61.22$; $H = 5.69$. $C_{10}H_8O_4$: NC_2H_5 requires $C = 61.28$; $H = 5.53$ per cent.

Analyses of the acid and of some of its derivatives have already been given in the paper referred to.

The fraction less soluble in water crystallised from concentrated solution in beautiful, colourless prisms which contained no water of crystallisation, and in an open capillary tube melted at 189—190°. The acid was dried at 100° for analysis:

0.2530 gave 0.4900 CO₂ and 0.1017 H₂O. C=52.82; H=4.46.
$$C_{10}H_{10}O_6$$
 requires C=53.09; H=4.42 per cent.

The methoxy-groups were determined by Zeisel's method:

0.2420 gave 0.4841 AgI.
$$OCH_3 = 26.42$$
. $C_6H_2(OCH_3)_2(COOH)_2$ requires $OCH_3 = 27.43$ per cent.

The crystalline residue obtained from this operation gave, with ferric chloride, the characteristic catechol reaction.

Silver Salt.—The normal silver salt was prepared by neutralising the acid with potassium hydroxide, and precipitating with silver nitrate. It was dried at 100° for analysis:

```
I. 0.3910 gave 0.1920 Ag. Ag = 49.10.

II. 0.3412 ,, 0.1678 Ag. Ag = 49.12.

C_{10}H_8O_6Ag_2 requires Ag = 49.09 per cent.
```

The potassium, barium, and lead salts and the acid silver salt are described in detail, and the analyses given under the name of salts of corydalinic acid in a previous paper (Trans., 1894, 65, 57).

The ethylimide of this acid was prepared by the method already described (Trans., 1895, 67, 19), and purified by repeated crystallisation from hot methylic alcohol, in which it was sparingly soluble. It melted sharply at 227°, and after drying at 100° gave the following numbers on analysis:

I. 0.2262 gave 0.5072 CO_2 and 0.1157 H_2O . C=61.14; H=5.67. II. 0.2805 , 14.5 c.c. nitrogen at 15° and 761 mm. N=6.16. $C_{10}H_8O_4$: NC_2H_5 requires C=61.28; H=5.53; N=5.96 per cent. **VOL. LXXV.**

This acid, therefore, is metahemipinic acid, and is identical with the variety of hemipinic acid obtained from papaverine. The following table indicates the properties of the two acids on which we have relied for their identification:—

	Hemipinic acid.	Metahemipinic acid.		
M. p. in open capillary tube. Solubility in water Reaction of a 1 per cent.	181°. Moderately soluble.	199°. Much less soluble.*		
solution: (1) with ferric chloride (2) with dilute solution of	Orange yellow ppt.	Cinnibar orange ppt.		
silver nitrate	No precipitate. 92°.	White crystalline ppt. 228°.		
Solubility of ethylimide in methylic alcohol	Very easily soluble.	Sparingly soluble.		

^{*} One part of metahemipinic acid requires for solution 130 parts water at 16.5°. The solubility of hemipinic acid is about twice that of metahemipinic acid at the same temperature.

These properties agree perfectly with those given by Goldschmiedt and Ostersetzer (*Monatsh.*, 1888, 9,762) for hemipinic acid (from narcotine) and metahemipinic acid (from papaverine) respectively. The melting, or, rather, decomposing points of the two acids vary very much with the rate of heating, and cannot be relied on as a means of identification.

The examination of the residue containing the mixture of hemipinic acids presented some difficulty, until the detection of metahemipinic acid amongst the products of decomposition of corydic acid led us to suspect its presence in the mixture. Once the presence of both acids had been ascertained, the separation was easily effected by fractional crystallisation as already described. It may also be accomplished by one or other of the following methods, which we found useful for freeing one acid from traces of the other: (a) precipitation with silver nitrate in dilute solution, which throws down metahemipinic acid, but not hemipinic acid; (b) conversion into ethylimides and treatment with methylic alcohol, in which the ethylimide of hemipinic acid is very easily soluble, whilst that of metahemipinic acid is only sparingly so. When a weighed quantity of metahemipinic acid is neutralised with ammonia, and a solution containing an equal weight of the acid is added, a sparingly soluble salt is obtained; the salt of hemipinic acid prepared in the same way is at least 20 times more soluble, and advantage can also be taken of this difference in solubility to effect the separation of the acids.

We have to express our indebtedness to Mr. R. D. Abell, of this College, for carrying out some of the analyses quoted in this paper.

The further examination of the products of oxidation with permanganate, as well as with nitric acid, is in progress.

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LXV.—The Relative Efficiency and Usefulness of various forms of Still-head for Fractional Distillation, with a Description of some new Forms possessing special Advantages.

By Sydney Young, D.Sc., F.R.S.

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WHEN a mixture of two liquids is distilled from an ordinary distillation bulb with a short, vertical still-head, the amount of separation effected by a single distillation is small unless the boiling points of the components are very far apart.

In order to bring about a satisfactory separation with such an apparatus, a series of systematic fractional distillations is necessary, and if the boiling points of the two liquids are near together, the number of distillations, and consequently the time required, is very great; indeed, the unavoidable loss of material by evaporation and by transference of liquid from one vessel to another may be so great as to render it impossible to separate either substance in a state of purity.

The object of the numerous modifications that have been made in

the still-head is to bring about a more complete separation of the components of the mixture in a single distillation, a process of fractionation—more or less effective according to the form of apparatus and the rate of distillation—taking place in the still-head.

Of all possible forms, the plain vertical still-head is the least efficient. During the distillation, as the vapour rises up the cylindrical tube, the outer parts of it come in contact with the condensed liquid flowing down the sides of the tube. Since the tube is constantly losing heat by radiation and by conduction to the surrounding air, this liquid is slightly cooled and fresh condensation constantly goes on, the outermost layer of vapour probably condensing pretty completely and with little change of composition. The central portion of vapour rises rapidly up the tube, and can only reach the liquid by diffusion or convection currents, and much of it may pass through the still-head without reaching the liquid at all; the condensed liquid, on the other hand, flows rapidly down the vertical walls of the tube back to the still. In order that the separation may be effective, however, the whole of the vapour should be brought well in contact with the condensed liquid, so that a state of equilibrium, as regards composition, may be brought about between them.

Let us suppose—to facilitate the consideration of what occurs—that Brown's law (Trans., 1880, 37, 49) holds good for the particular

mixture distilled; that is to say, that $\frac{x_1}{x_2} = C \frac{w_1}{w_3}$ where x_1 and x_2 are

the weights of the two substances in the vapour at any moment, w_1 and w_2 the weights in the liquid in contact and in equilibrium with the vapour, and C a constant depending on the substances employed. Also, for the sake of simplicity, let us suppose that, in the first place, equal weights of the two substances are taken, so that $w_1 = w_2$, and that C = 2.

Then the composition of the first small quantity of vapour formed is given by the equation $\frac{x_1}{x_2} = 2$, and the percentage composition will

If a distillation bulb with exceedingly short still-head be used, this will practically be the composition of the distillate first collected.

be $x_1 = 66.7$, $x_2 = 33.3$.

Suppose, now, that in the lower part of a longer and theoretically perfect still-head condensation goes on and that the condensed liquid remains in the tube until its weight is, say, 50 times as great as that of the residual uncondensed vapour in the tube, the total weight of vapour and liquid being, say, 1/1000 of that of the mixture taken. We may then assume (1) that the composition of the liquid and vapour in the still-head (taken as a whole) will be practically the

same as that of the vapour first formed, and (2) that the composition of the condensed liquid will differ but very slightly from this, or $\frac{w'_1}{w'_2} = 2$.

If the residual vapour is brought into thorough contact with the condensed liquid, its composition will practically be given by the equation $\frac{x'_1}{x'_2} = 2 \times 2$, and its percentage composition will be $x'_1 = 80$, $x'_2 = 20$.

If we suppose, as a theoretical case, that the still-head is divided into 10 sections and that the distillation goes on in such a manner that perfect equilibrium between vapour and condensed liquid is established in each section, and, lastly, that the condensed liquid in any section has the same composition as the vapour in the section below, then we should have for the composition of the vapour in the 10 sections when the distillate first begins to be collected

Number of section.	Percentage compo	age composition of vapour.				
	$\pmb{x_1}$	$oldsymbol{x_2}$				
1	80.0	20.0				
2	88.9	11.1				
3	94.1	5.9				
4	97.0	3.0				
5	98.5	1.5				
6	99.2	0·8				
7	99.6	0.4				
8	99.8	0.2				
9	99-9	0.1				
10	99-95	0.05				

Such an arrangement is not realisable in practice, but our aim should be to approach as closely to it as possible.

In choosing—or constructing—a still-head, the first point to be considered is its efficiency in separating the components of a mixture. It frequently happens, however, that the quantity of liquid available is small, and in any case, when a series of fractional distillations has to be carried out, some of the fractions usually become very small. In such a case, of two still-heads of equal efficiency, that one is the more useful which allows of the distillation of the smaller quantity of liquid. Now in any still-head a certain amount of condensation is constantly going on and the condensed liquid flows back into the still; at any moment there is necessarily a certain amount of condensed liquid in the still-head, and, obviously, the smallest quantity of a substance that can be usefully distilled must be considerably greater than that of the liquid and vapour in the still-head. It is therefore

of great importance to construct the still-head in such a manner that—consistently with efficiency—the quantity of condensed liquid in it at any moment shall be as small as possible. Among other points to be considered are (1) ease of construction and cheapness, (2) freedom from liability to fracture, (3) convenience in handling.

The object of the investigation described in this paper was to ascertain what form of still-head gives the best results, not only as regards efficiency, but in other respects.

DESCRIPTION OF EXPERIMENTS.

In making such a comparison, it is, of course, necessary always to distil a mixture of the same composition; equal weights of benzene and toluene—both of quite constant boiling point—have been employed throughout.

In the earlier experiments, the rate of distillation was regulated by occasionally counting the number of drops of distillate per minute and adjusting the flame so as to make this number about 60. It was soon found, however, that the rate of distillation has a very marked influence on the result, and that, to ensure a fair comparison, it would be necessary to regulate the rate more carefully; a seconds pendulum was therefore made to swing behind the receiver in which the distillate was collected, and it was thus much easier to time the drops during the whole process.

Unless otherwise stated, the rate was one drop of distillate per second.

Only three of the earlier experiments—those in which 400 grams of the mixture were distilled—are referred to in this paper.

That the rate of distillation does greatly influence the separation is well shown by the table on p. 683, in which are recorded the results of three distillations, each of 50 grams of the mixture, at the rates of 30, 60, and 120 drops per minute, with a Young and Thomas dephlegmator having three constrictions.

The distillate was collected in 11 fractions, the 12th consisting of the residue (calculated by difference) after the boiling point had reached that of pure toluene.

For convenience, the results are stated in percentages. It will be seen that a very much better separation is effected by diminishing the rate of distillation.

The weight of vapour and condensed liquid in the still-head during the distillation (p. 681) was arrived at in the following manner: The distillation was continued as nearly as possible to the last drop and, after cooling, the liquid in the flask (still) and, when possible, in the still-head, was weighed. The sum of these two weights gives the

TABLE I.

	Number of drops of distillate per min				
Temperature range.	80	60	120		
	Percent	Percentage weight of distill			
80·2 83·2	0.8	0.6	0.6		
83.2— 86.3	29.6	21.8	10.8		
86:3— 89:4	9.8	14.3	20.2		
89.4— 92.5	5.6	7.8	12.6		
92.5— 95.6	3.8	5.0	7.0		
95.6— 98.7	3.0	4.7	5.4		
98.7—101.8	2.8	4.0	5.0		
101.8—104.8	8.0	3.6	5.0		
104:8—107:9	4.3	5.2	5.6		
107·9—110·8 110·3—110·9	6.2	7.3	9.2		
Pure toluene, by difference	11·6 19·5	9·8 15·9	11.0		
i die toldene, by dinolence	19.0	10.9	7.0		
	100.0	100.0	100.0		
	_		-		
Percentage weight of distillate below 95.6°.	49.6	49.5	51-2		

^{*} Temperature barely reached 110.9°; residue not quite pure toluene, boiling (from ordinary bulb) at 110.8—110.9°.

amount of liquid and vapour in the still-head and flask when the flask contained the smallest possible quantity of liquid. As the same (round-bottomed) flask was used throughout, except for the distillation of 400 grams of the mixture, and as the substance in the still and still-head at the end of the distillation always consisted of pure or nearly pure toluene, the weight of liquid and vapour in the flask may be taken as constant and was estimated to be 0.85 gram. The values given in tables II, IV and V for the weight of liquid and vapour in the still-head have been obtained as a rule by subtracting 0.85 gram from the weights of liquid (after cooling) in the still-head and flask.

In some cases, it was not possible to weigh the residual liquid in the still-head after cooling, but a fairly accurate estimate of the weight of liquid and vapour in the still-head during the distillation could be obtained in the following manner. After the distillation had been carried as far as possible, the distillates were weighed; the difference between the weight of the mixture taken and the total weight of distillate represents the weight of liquid and vapour in the flask and still-head plus the loss by evaporation. This loss was directly deter-

mined in many cases, and was found to vary within small limits (0.0 to 0.65 gram; mean of 27 observations, 0.25 gram), being somewhat greater with the larger still-heads than the smaller ones. The estimated loss by evaporation +0.85 was subtracted from the difference between the original weight of mixture and that of the combined distillates, and this was taken as the required values.

The weight of mixture distilled was, unless otherwise stated, 50 grams; the fractions were collected, as a rule, with temperature ranges of 3.0° or 3.1°, except near the boiling point of toluene, where the intervals of temperature were reduced to 2.4° and 0.6°, for it is a general law, so far as I know without exception, that the less volatile of the two components of a mixture is more easily and quickly separated than the more volatile.

The following data relating to each still-head are given in Table II (p. 685):—

- 1. The vertical height of the still-head measured from the bottom to the side delivery tube in cm.
 - 2. The approximate internal surface in sq. cm.
 - 3. The percentage weight of distillate.
- 4. The weight of vapour and condensed liquid in the still-head during the distillation when pure or nearly pure toluene was coming over (see p. 683).
- 5. The percentage weight of distillate collected below the middle temperature, 95.6°; this is a point that will be referred to later.

The nature of each still-head is indicated at the top of the column and it is numbered below for convenience of reference.

The Plain Vertical Still-head.

Although the plain vertical still-head is less efficient than any other, yet a certain amount of fractionation does take place in it, and some experiments were made to ascertain the effect of altering the length and the diameter of the tube.

The influence of alteration of length is seen in distillations I to III. As might be expected, the efficiency is improved by increasing the length of the tube; the weight of vapour and liquid also increases with the length, but somewhat more rapidly.

For tubes of (approximately) equal length, the efficiency does not bear so simple a relation to the width, as will be seen by comparing the results of distillations IV, V, II, VI, VII.

Starting with the narrowest tube,* as the width increases the

* A short piece of wider tubing (3 or 4 cm. long and 10 or 12 mm. wide) should be fused to the lower end of the very narrow tubes, which might otherwise become blocked with liquid.

efficiency falls, reaches a minimum, and then rises again. Thus the tube of medium width (II) is the least efficient of the five, at any rate as regards the separation of benzene, and is very decidedly less efficient than either the very narrow or the very wide tube. The very narrow tube gives a slightly better result than the very wide one, although the internal surface of the wide tube is four times as great as that of the narrow one, and the weight of liquid and vapour in the still-head three times as great. In making a plain still-head, it is therefore clearly more advantageous to use very narrow tubing than very wide.

It is remarkable that the ratio of the weight of vapour and liquid in the still-head to the internal surface is greatest in the case of the narrowest tube, falls to a minimum with the tube of medium width, and then rises slowly again with the wider tubes; the actual values are: 0.0081, 0.0062, 0.0057, 0.0062, 0.0066. The rise of the ratio with the wider tubes is due, partly, at any rate, to the fact that the capacity of the tubes, and therefore the weight of vapour in them, varies as the square of the radius, whilst the surface varies directly as the radius. On the other hand, the rise with the narrower tubes is probably due to the retardation of the downflow of condensed liquid by the uprush of vapour, the upward velocity of the vapour varying inversely as the square of the radius. The effective radius is not, however, that of the tube itself, but is diminished by the layer of liquid, which increases in depth from top to bottom of the tube. That this is the true explanation seems to be borne out by the fact that it was impossible to carry out a distillation with a slightly narrower tube (internal diameter, 4.2 mm.), owing to the liquid actually joining up into columns near the bottom of the tube when the temperature had reached about 100°.

A few experiments were made to ascertain the effect of increasing or diminishing the loss of heat:

- (a) By blackening the outer surface of the tube to increase radiation.
- (b) By covering the tube with bright tinfoil to diminish radiation.
- (c) By covering the tube thickly with cotton wool to diminish conduction to the surrounding air.

A comparison of distillations II, VIII, IX, and X shows that the quantity of liquid in the still-head is very slightly increased by blackening the tube, and is very slightly diminished by covering it with tinfoil. The diminution is more marked when the tube is covered with cotton wool, but the weights vary only between 1.6 and 1.3 grams. The efficiency is slightly lowered in the last case, but in the others the differences are quite within the limits of experimental error.

A more marked effect was produced by covering a tube, with 13 bulbs blown on it, with cotton wool; in that case, the weight of vapour and liquid in the still-head fell from 3:55 to 2:65, and the efficiency

was noticeably diminished, although by no means to a corresponding extent.

In the distillation of liquids of high boiling point, it would, perhaps, be advantageous to cover the still-head with a good non-conductor, as the quantity of condensed liquid rises rapidly with the boiling point of the liquid distilled.

In Tables II, IV, and V, the percentage weight of distillate collected below the middle temperature, 95.6°, is given, and it will be seen that, with the plain vertical still-heads, the percentage is uniformly lower than 50—varying from 45.4 to 48.5—whereas, with the still-heads modified in the most various ways so as to increase the efficiency, the percentage in nearly every case differs but slightly from 50. Omitting the distillations of 25 grams of the mixture, the percentage varied from 47.9—52.0. This may, perhaps, be taken as a further indication of the inferiority of the plain vertical still-head.

Regulated Temperature Still-head.

If the still-head is surrounded by water kept at a temperature as little above the boiling point of the more volatile component as will allow of vapour passing through, a considerable improvement is effected in the separation; but the temperature of the bath requires very careful regulation, for if the boiling points are near together, or when one component is present in large excess, a fall of a fraction of a degree would condense the vapour completely, and a rise of temperature to a similar extent would prevent any condensation from taking place, and fractionation would be impossible.

When a regulated temperature still-head is employed, it is better, for two reasons, to bend the tube into the form of a spiral; in the first place, the effective length of the still-head is thereby greatly increased without unduly increasing the height of the bath; and, in the second place, as will be seen later, for a given tube the spiral form is more efficient than the vertical.

The regulated temperature still-head is specially useful for very volatile liquids; by employing a combination of such a still-head with a dephlegmator, it was found possible to separate normal and iso-pentane (b. p. 36.3° and 27.95° respectively) in a state of purity from a light distillate from American petroleum (Young and Thomas, Trans., 1897, 71, 440). I have also found the same arrangement very useful in the partial separation of the hexanes and pentamethylene from petroleum.

The experimental difficulties increase rapidly, however, as the temperatures rises, and I do not think that the regulated temperature still-head will ever be largely used for liquids boiling above 70° or 80°.

I have not made any comparison of a still-head of this class with the others, because it would be exceedingly difficult, if not impossible, to regulate the temperature of the bath and at the same time the supply of heat to the still so as to keep the rate of distillation even approximately constant.

Winssinger's apparatus (Ber., 1883, 16, 2640) belongs to the class of regulated temperature still-heads; a current of water passes, however, through a double tube placed inside the vertical still-head. Claudon (Bull. Soc. Chim., 1884, 42, 613), states that Winssinger's apparatus is improved by surrounding the inner tube with wire gauze; this would, no doubt, be the case.

The great drawback to this form of apparatus, whether the current of water is internal or external, is the necessity for constantly and carefully regulating the supply of heat both to the still and to the water. F. D. Brown (Trans., 1880, 37, 57) has devised an arrangement by which the spiral still-head is heated by means of a bath of a suitable liquid boiling under reduced pressure. The temperature being thus regulated by the pressure under which the liquid is boiling, would certainly be under much better control.

MODIFICATIONS OF THE STILL-HEAD.

Sloping and Spiral Still-heads.

It has been pointed out that the inefficiency of the plain vertical still-head is due to the want of thorough contact between the vapour and condensed liquid, owing, firstly, to the central portion of the vapour passing rapidly up the tube and, possibly, never meeting with the liquid at all, and, secondly, to the condensed liquid flowing down very rapidly away from the vapour back into the still.

Any modification of the still-head that brings about better admixture of the ascending vapour or that retards the downflow of condensed liquid should therefore increase its efficiency.

The simplest and most obvious alteration that can be made is to alter the slope of the tube so as to retard the downflow of liquid. This may be done by bending the tube near the bottom and top, at an angle slightly greater than a right angle, so that the ends of the tube remain vertical but the middle part slopes very gently upwards. By comparing the results of distillations V and XI, it will be seen that a notable improvement, especially in the separation of benzene, is actually brought about by this alteration; at the same time, it is remarkable that the quantity of liquid in the still-head is slightly diminished.

The efficiency is further improved by bending the sloping portion of the tube into the form of a spiral, probably because a better admixture of the vapour is thus produced; this will be seen by comparing V, XI, and

F10. 1.

XII, and also IV and XIII. Here, again, although the vertical height through which the condensed liquid had to flow was less than half of

what it was when the tubes were vertical, yet the amount of liquid in the still-head was diminished in each case by 0.2 gram.

It is clear, then, that both efficiency and usefulness are increased by bending the tube into the form of a spiral.

Rod and Disc Still-head.

An arrangement was next tried in which a portion of the condensed liquid was greatly retarded in its downflow and was not exposed to the cooling action of the air; at the same time, eddies and cross-currents were produced in the ascending vapour.

By heating a small part of a glass rod in the blow-pipe flame and, when quite soft, pressing the glass together, it is forced out into the form of a nearly flat disc. Twenty of these discs were made on a long glass rod, and at each end of the rod a little tripod of glass was fused. The tripods serve to centre the rod and the lower one rests on the constricted part of the vertical still-head (Fig. 1).

The rod with the discs was placed in the plain tube used for distillation II (the tube itself was very inefficient, being of medium width), and the distillation with this apparatus is numbered XIV.

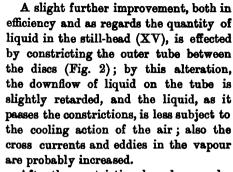
When the distillation commenced, condensation took place, of course, not only on the outer tube, but also on the rod and discs, and it was found that throughout the distillation the discs remained covered with a thin layer of liquid, the downflow of which must have been exceedingly slow.

The increase of efficiency with this apparatus is very marked; the results obtained—when the same quantity of liquid is distilled—are, indeed, better than those given by the 3-bulb Le Bel-Henninger and much better than those with the 3-bulb Glinsky dephlegmator (Table IV, p. 702), and the apparatus has the additional advantage of being easily constructed and very convenient to handle; it is not at all liable to fracture, and can be used for

the distillation of much smaller quantities of liquid than the dephlegmators referred to.

The quantity of vapour and liquid in the still-head, 2.35 grams, is the same as that in the wide tube, VI, but the efficiency is very much greater.

Fig. 2.



After the constrictions have been made, however, the rod with the discs cannot be taken out of the tube, and it is perhaps doubtful whether the moderate increase in efficiency is sufficient to make up for this drawback in addition to the slightly greater difficulty of construction.

That the apparatus—and the same remark would apply to the tube without constrictions—can be advantageously employed for the distillation of much smaller quantities of liquid than the ordinary 3-bulb Glinsky or Le Bel-Henninger dephlegmators, and that it is superior in this respect to the 3-bulb Young and Thomas dephlegmator, may be seen by referring to Table IV, p. 702.

Bulb Still-head.

Wurtz (Ann. Chim. Phys., 1854, [iii], 42, 129) recommends a vertical tube with a series of bulbs blown on it, and this arrangement is usually considered specially suitable for liquids of high boiling point.

Distillations XVI, XVII, and XVIII were carried out with still-heads consist-

ing of vertical tubes with 3, 7, and 13 bulbs respectively; the average diameter of the bulbs was 3.42 cm.

Distillation XVI, with the 3-bulb tube, may be compared with III V, and VI; the results are very similar to those with the narrow plain tube, V, and the quantity of vapour and liquid in the stillhead is only slightly less; it is, however, much less than with the long or wide tubes III and VI.

The 7-bulb tube, XVII, gives a slightly better separation than the very narrow tube bent into a spiral, XIII, but the quantity of vapour and liquid in the still-head is twice as great. The very narrow tube of spiral form is therefore to be preferred.

The tube with 13 bulbs, XVIII, is more efficient than the plain tube with the rod and discs, XIV, or the same tube with the constrictions between the discs, XV. On the other hand, the quantity of vapour and liquid in the still-head is rather more than half as large again. Comparing the rod and disc still-head, XIV, with the 7-bulb tube, XVII, it will be seen that the increase in efficiency is relatively greater than the increase in the quantity of liquid and vapour in the still-head; the rod and disc tube may therefore be recommended in preference to the bulb-tube. Comparing the bulbtubes together, it is seen that the efficiency increases regularly with the length and the number of bulbs. It would hardly have been necessary to make the experiments to prove this point were it not that Kreis (Annalen, 1884, 224, 259) makes the statement—quoted without comment in some recent standard works on chemistry—that a Wurtz tube with 4 bulbs gives no better results than one with 2 bulbs of the same size, and that a tube with 4 bulbs gives about the same result as one of the same diameter as the bulbs.

Kreis states that he distilled in each case a mixture of 25 grams of benzene and 25 grams of toluene, and compared, amongst others, an ordinary distillation bulb, a 2-bulb and a 4-bulb Wurtz tube (bulbs the same size), and a vertical tube of the same width (except at top and bottom) as the bulbs in the Wurtz tubes. The quantities of the distillates are given in c.c., so that the 50 grams would correspond to rather less than 60 c.c. (the temperature was presumably that of the laboratory at the time).

Kreis carried out 12 fractional distillations with the ordinary distillation bulb and 6 with each of the other tubes. Table III (p. 692) the first two distillations with the ordinary apparatus, and the first only with the others.

There are several points about these results which it seems impossible to explain. In the separation of two liquids by fractional distillation, so far as my experience goes, the highest and lowest fractions invariably increase with each distillation, and this is also the case with the great majority of the fractionations carried out by Kreis. second distillation with the ordinary, apparatus, the highest fraction

TABLE III.

Nature of still-head.	Ordinary distillation bulb. First distillation.	Ordinary distillation bulb. Second distillation.	Wurtz tube with 2 bulbs.	Wurtz tube with	Plain tube of same width as bulbs in Wurtz tubes.		
Temperature range.	Volume in cub. cm.						
81— 84 84— 87 87— 90 90— 98 93— 96 96— 99 99—102 102—105 105—108 108—111	0·0 0·0 1·0 12·5 13·5 4·0 4·5 4·0 2·5 17·0	0·0 2·5 7·5 8·0 7·0 9·0 8·5 7·0 4·0 3·0 56·5	1·0 10·0 14·5 8·0 5·5 2·5 3·5 3·5 3·5	0.0 0.0 5.0 13.5 8.0 5.5 4.5 5.0 4.0 14.0	0.0 0.5 4.5 14.0 11.0 5.5 5.5 4.0 3.5 9.0		
Percentage of distillate collected up to 96°, taking the total original volume as 60 c.c.	45.0	41.7	65-8	44.2	48.8		

(108—111°) fell from 17 c.c. to 3 c.c. One would naturally suppose that there was a misprint, but the total volume is about right in each case, and I see no way of getting over the difficulty. The results given for the remaining 10 distillations agree with those of the second, which may, therefore, be probably taken as the more correct, although 3 c.c. is an exceedingly small quantity for the highest fraction unless the distillation was taken very rapidly.

Again, in Tables II, IV, and V in this paper, it will be seen that the percentage weight of distillate collected below 95.6° varies only between 45.4 and 52.0, or, excluding the results with the plain vertical still-heads and those obtained when only 25 grams of the mixture were distilled, between 47.9 and 52.0. Yet in the distillation carried out by Kreis with the 2-bulb Wurtz tube, the percentage is 65.8 and with the 4-bulb tube it is 44.2, the one far too high and the other certainly too low for such a tube.

If the experimental results obtained by Kreis were to be accepted as even fairly accurate, one would have to conclude that a 2-bulb Wurtz tube gives an incomparably better separation of benzene but a very much worse separation of toluene than the 4-bulb tube. Cer-

tainly, the conclusion arrived at by Kreis that the results are very similar are not justified.

It will be noticed also that the results of the distillation with the 4-bulb Wurtz tube are somewhat similar to those of the first distillation with the ordinary distillation bulb; such a result could only be arrived at by taking the one distillation very rapidly and the other very slowly.

The "Pear" Still-head.

The Wurtz still-head may be improved—to some extent in efficiency but chiefly by diminishing the quantity of condensed liquid—by heating the upper part of each bulb in the blow-pipe flame and then pushing down the narrow connecting tube, so as to give to each bulb what may be roughly described as the

give to each bulb what may be roughly described as the form of a pear (Fig. 3). The result of this alteration is that the condensed liquid in any bulb, after flowing down the constrictions, instead of spreading itself over the inner surface of the bulb below, mixing with the liquid condensed in that bulb and flowing down the sides with increasing velocity, collects on the depression in the bulb below and falls in drops near the middle of the bulb. The liquid on the inner surface of each bulb is merely that condensed in that bulb, and its velocity of downflow is no greater in the bottom bulb than the top one. The liquid, on the other hand, that collects on a depression (that is to say, the total quantity condensed in the part of the still-head above it) is brought well in contact with the ascending vapour in a part of the bulb that is less exposed to the cooling action of the air than any other. It is probable, also, that the eddies in the vapour are greater than in the ordinary bulb tube.

This form of tube is hardly more difficult to construct than the Wurtz tube, and certainly possesses considerable advantages over it. It is more efficient than the rod and disc still-head of the same length, and the amount of vapour and liquid is only slightly greater; it is, however, perhaps not quite so easy to

construct. The "Pear" still-head may be recommended above all others for the distillation of liquids of high boiling point.

The Hompel Still-head.

Of the other still-heads belonging to this class, the only one in common use requiring special mention is that devised by Hempel VOL. LXXV.

(Zeit. anal. Chem., 1881, 20, 502). Its great advantages are efficiency and ease of construction; its great disadvantage is the excessive amount of condensed liquid in the still-head, which makes it unsuitable for the distillation of small quantities.

Hempel describes his apparatus pretty much as follows: A straight, wide vertical tube is used and a constriction is made in it near the bottom. The beads (about 4 mm. in diameter) arrange themselves naturally over the constriction in the form of a dome (gewölbartig) and remain quite securely, even when the liquid being distilled boils with bumps. A short, narrower, vertical tube with side delivery tube is fitted by means of an ordinary cork into the wide tube containing the beads.

There are two points in connection with this description to which it may be well to call attention.

The setting of the beads into the form of a dome is very important, because, if the constriction were made narrow enough to prevent the beads (even larger ones) from falling through, and if they were allowed to rest in the constriction, the tube would become filled below with condensed liquid and thus the amount of liquid in the still-head would be greatly increased, and the distillation might have to be occasionally interrupted.

I prevented the beads (which were larger and of the special form now supplied for the Hempel tube) from reaching the constriction by

causing them to rest on a flat glass star, made by fusing together three pieces of glass rod, each bent at an angle of 60°.

F10. 4.



I adopted Hempel's plan of connecting a short narrow vertical tube by means of a cork with the wider tube containing the beads. This is better than sealing the upper narrow tube to the wide one (which is sometimes done), because the liquid that condenses in the narrow tube (I blew a small bulb

on the tube to slightly increase the condensation) falls on to the top beads and ensures their being thoroughly moistened with liquid. If the upper tube is sealed to the wide one, the condensed liquid flows down the side and only reaches the beads lower down.

The "Evaporator" Still-head.

The importance of reducing as far as possible the amount of condensed liquid in the still-head led me to consider whether it would not be possible to devise an apparatus in which a considerable part of the condensed liquid should be reconverted into vapour, very thorough contact being at the same time established between the liquid and vapour. The apparatus described below, which may be called the "evaporator" still-head, was finally adopted as the one giving the best results.

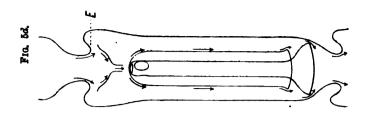
The general form of the apparatus is shown in Fig 5a (p. 696), and one of the sections on a larger scale in Fig. 5b. Each section consists of three separate parts; (1) the outer tube, A, 22—24 mm. internal diameter, connected above and below with other sections; the bottom one, however, connected below with the pear-shaped bulb A_1 , and the narrow tube A_2 ; the top one connected above with the bulb A_3 and the narrower tube with the side delivery tube A_4 . The construction of this part is clearly indicated by the diagram. The length of a section should be about 10 or 10.5 cm.

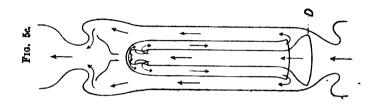
- (2) An inner thin-walled tube, B, 7.5—8 mm, internal diameter and 60 mm, long, open at each end and widened below into the form of a funnel which rests on the constricted part of A, and should fit it fairly accurately. Two holes, B₁, are blown in the sides of B near the top.
- (3) An intermediate tube, C, about 14 mm. internal diameter and 50 mm. long, like a small, inverted test-tube. Above the tube C, and attached to it by the three glass legs shown in Fig. 5b, is a small funnel, C_1 , which must be a little wider than the depression in the tube A just above it. The tubes B and C are centred and kept in position by the little glass projections shown in the same figure.

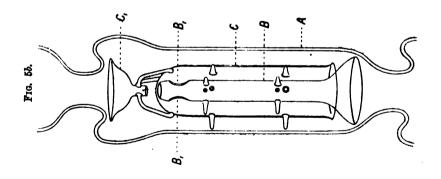
The upward path of the vapour is indicated by the arrows in Fig. 5c. The narrow passage, D, where the inner tube rests on the constriction in the outer one, becomes at once blocked by condensed liquid, and the vapour therefore rises up the inner tube and passes through the openings at and near the top of it, then down between the inner and middle tubes and up again between the middle and outer tubes. It then passes round between the funnel and the depression at the top of the outer tube, and finally up into the next section above.

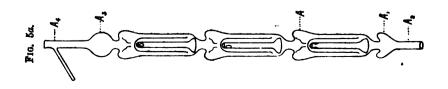
The downward path of the main body of condensed liquid is indicated by the arrows in Fig. 5d. The whole of the liquid condensed in the still-head above any section collects together and flows down the walls until it falls in drops from the depression, E, into the funnel. From this it falls on to the top of the middle tube and spreads itself over its surface, falling again in drops from the bottom of this tube, and finally passing between the bottom of the inner tube and the constriction in the outer one on which the inner tube rests, and thus into the section below. There is no difficulty in making the inner tube fit the outer one with sufficient accuracy to prevent the vapour passing up, but without interfering with the free downward passage of the condensed liquid.

At the same time, fresh condensation is going on in each section on









the inner walls of each of the three tubes, mainly, of course, on those of the outer tube, which is exposed to the cooling action of the air.

When a mixture is being distilled, wherever partial condensation takes place and the residual vapour comes well in contact with the liquid, an alteration in composition takes place, such that the vapour becomes richer in the more volatile component; at the same time, a corresponding fall in temperature occurs, the condensing point being lower than that of the original vapour. Thus in any section of the still-head the vapour ascending through the inner tube will be hotter than that descending between the inner and middle tubes, and this again will be hotter than that rising between the middle and outer tubes. As the temperature of any tube tends to become the mean of the temperatures on either side of it, there will be some condensation on the inner wall of each tube and some excess of evaporation—if liquid is present—from the outer wall of the inner and middle tubes. When the amount of liquid flowing over the outer surface of the middle tube is small, and especially when the two components of the mixture differ considerably in volatility and are present in fairly equal quantity, the evaporation of the liquid is quite easily observed. Under the last named conditions, there is a tendency for the drops from the little funnel to assume the spheroidal state and to rebound from the middle tube and strike against the walls of the outer tube, where they at once coalesce with the liquid which is there being condensed.

When a pure liquid, on the other hand, is being distilled, there is no temperature difference between the three concentric tubes, and the spheroidal state is not assumed after the whole still-head is thoroughly heated until near the end of the distillation, when the vapour in the still may be superheated, the spheroidal state being then seen in the lowest, and possibly to a slight extent in the second, section. doubt the amount of evaporation from the middle tube is diminished to a certain extent by some of the drops simply rebounding from its surface and failing to wet it, but the formation of spheroidal drops may be easily prevented by fusing to the top of the tube a fine needle of glass of such a length that it reaches or just passes up through the bottom of the little funnel. The needle is indicated by the dotted line in Fig. 5b.

Distillations XXI and XXII were carried out with "evaporator" still-heads (without the glass needles) with 3 and 5 sections respectively. Comparing the results of XXII with those obtained with the Hempel tube, XX, it will be seen that, whilst the separation is very much better, the weight of vapour and liquid in the still-head is less than two-thirds as great.

For a given efficiency, the "evaporator" still-head is also superior

to the Glinsky or Le Bel-Henninger dephlegmators, or to that devised by Thomas and myself (see Table IV, p. 702), and it may therefore be most strongly recommended for the purification of small quantities of liquid of moderate boiling point. It has the further advantages that it is constructed entirely of glass; that it is convenient to handle; that it can be held in any position without danger of breakage or getting out of order; lastly—and this is important—after the distillation is over, practically the whole of the liquid returns from the still-head to the still; thus, with the "evaporator" still-head with 5 sections the amount of toluene left in the still-head was only a small fraction of a gram, and with more volatile liquids the amount was almost inappreciable. The one disadvantage is the difficulty of construction.

The "Dephlegmators" of Glinsky, Le Bel-Henninger, and Young and Thomas.

Probably the still-heads most frequently used in the laboratory are those of Glinsky and Le Bel-Henninger: they and also that of Young and Thomas differ somewhat widely from those which have been so far considered.

The principle on which they are constructed is common to many of the dephlegmators which have long been employed on the large scale for the purification of alcohol, benzene, and other liquids. It may, perhaps, be convenient to reserve the term "dephlegmator" for this particular class of still-head. In these dephlegmators, the return flow of condensed liquid is obstructed at definite levels in the vertical still-head, so that the liquid collects into a pool at each level, and the ascending vapour is compelled to force its way through the pool, thus bringing about very complete contact between vapour and liquid.

There is a fall of temperature from section to section from below upwards, caused partly by the change in composition and partly by the difference of pressure equivalent to the force exerted by the vapour in passing the obstruction. This difference of temperature brings about some re-evaporation of the liquid in the pools.

The first dephlegmator employed in the laboratory was that of Linnemann (Annalen, 1871, 160, 195). A number of cones of platinum gauze were placed at different heights in the vertical still-head and the liquid collected in these, some of it, however, finding its way past the cones and returning to the still. The drawback to this apparatus is that the liquid gradually accumulates in the still-head until the quantity becomes unmanageable and then the distillation has to be discontinued until the liquid returns to the still. The frequent interruption of the distillation is a source of annoyance and

loss of time, besides which it is very difficult to make an accurate record of the temperature. The apparatus is also unsuitable for the distillation of small quantities of liquid.

The difficulty has been overcome in the more recent dephlegmators, but Kreis (loc. cit.) looks upon the interruptions as rather an advantage than otherwise, on the ground that the vapour left in the still-head, which he considers would be very rich in the more volatile component, would be driven forward when the distillation was recom-I am unable to agree with this opinion.

To prevent accumulation of liquid in the pools, reflux tubes are required to allow the excess of liquid to flow back from bulb to bulb or into the still. It will be seen from what follows that the efficiency and usefulness of the various dephlegmators depend to a large extent on the size and arrangement of the reflux tubes.

In the Glinsky dephlegmator (Ann. Chem. Phys., 175, 381), the obstruction is caused by placing spherical glass beads over the constrictions between bulbs blown on the vertical tube; there is only one reflux tube carrying off the excess of liquid from the top bulb to the tube below the lowest bulb-practically back to the still,

In the Le Bel-Henninger dephlegmator (Ber., 1874, 7, 1084), the obstruction is usually caused by placing platinum cones in the constrictions between bulbs blown on the vertical tube; each bulb is connected by a reflux tube with the one below it, so that the liquid is carried back from bulb to bulb, and not straight to the still.

The Young and Thomas tube has been shortly described (Chem. News, 1895, 71, 177), and has given very good results, but is open to the objection that, in the form there given, it cannot be inverted without danger of getting the reflux tubes and obstructions permanently out of position. It was therefore unsafe to send the apparatus by rail in the ordinary way.

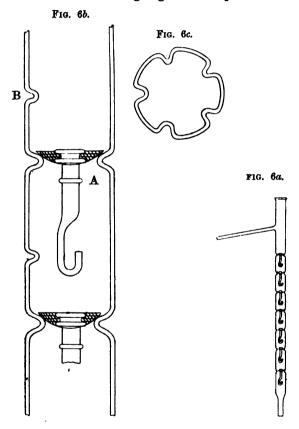
Modification of the Young and Thomas Dephleamator.

I have recently introduced two simple modifications which, whilst hardly appreciably increasing the difficulty of construction, enable the apparatus to be held safely in any position. The dephlegmator consists of a long glass tube (Fig. 6a, p. 700) of about 17 mm. internal diameter with the usual narrow side delivery tube. In the wide tube are a series of sharp constrictions on which rest concave rings of platinum gauze, and these support small glass reflux tubes of the form shown The upper and wider part of the reflux tube has an internal diameter of 4.5 mm., the narrow, U-shaped part, which serves as a trap, an internal diameter of 3 mm.; if, however, the number of constrictions exceeds 10 or 12, the traps for the lower reflux tubes

should be slightly wider, say 3.5 mm. The length of the reflux tubes should be about 45 mm., and the distance between two constrictions from 55 to 70 mm.

The enlargement, A, in the reflux tube is made after the platinum ring has been passed round the trap and up to the upper enlargement; it prevents the reflux tube from slipping through the ring if the tube is inverted.

The reflux tube and the ring together are prevented from falling



out of position when the tube is inverted by the five internal projections, one of which, B, is shown in Fig. 6b. A horizontal section through the tube at B is shown in Fig. 6c.*

* It has been suggested to me by Mr. C. E. Müller, of High Holborn, that the reflux tube might be made with a much wider rim at the top, so that this, and not the delicate platinum ring, would come in contact with the projections when the tube was inverted. This would, I think, be an improvement, and, with this alteration, three projections should be sufficient.

To give the platinum ring a concave form, I find it best to soften the gauze by heating it in the blow-pipe flame. By gently pressing down the reflux tube when the ring which supports it rests on a constriction in the wide tube, the ring takes the required form.

In constructing the apparatus, I find it best first to cut from the wide tube as many pieces (from 55 to 70 mm. long) as there are to be constrictions in the dephlegmator. The constriction is then made in each short tube separately, and a bad one may, of course, be rejected and a fresh piece cut off the tube. As the reflux tubes are also made separately, failure with any one part does not spoil or endanger the success of the still-head as a whole.

The subsequent fusing together of the short tubes is not difficult, and it is almost as easy to make a dephlegmator with 12 or 18 constrictions as with only 3 or 4.

The internal projections (B, Fig. 6b, and Fig. 6c) may be made with a carbon pencil immediately after sealing the short tube with the constriction to the part of the still-head that has been already completed.

Comparison of the Dephlegmators of Glinsky, Le Bel-Henninger, and Young and Thomas (modified).

In the first comparison of the dephlegmators—each with three obstructions and pools of liquid—400 grams of the mixture of benzene and toluene were distilled, and the rate was kept roughly at 60 drops per minute. In the second comparison, 50 grams of the mixture were distilled, and in the third 25 grams. In these cases, the rate was carefully regulated at 1 drop per second by reference to the seconds pendulum.

The results are given in Table IV (p. 702). It will be noticed that the Young and Thomas dephlegmator was a little longer * than the Le Bel-Henninger, and considerably longer than the Glinsky, and in that respect it had a slight advantage over them as regards separation.

Taking first the comparisons with 400 grams of the mixture, XXIII, XXVI, XXIX, the differences are not very marked, and may, perhaps, be partly accounted for by want of uniformity in the rate of distillation, and by the difference in length and width of the tubes. The Le Bel-Henninger tube, however, certainly gave a somewhat better separation of benzene than the others, and the Glinsky a decidedly worse separation of toluene.

The second comparison, XXIV, XXVII, and XXX, with 50 grams of the mixture, is a fairer one, in so far that the rate of distillation was very carefully regulated throughout by help of the seconds pendulum. It is also important as affording evidence regarding the

^{*} It might have been made much shorter.

TABLE IV.

																			1
Nature of still-head.	Glinsk mator	Hinsky dephieg- mator, 3 bulbs.	be .	Le Ba lephle	Le Bel-Henninger dephiegmator,3 bulbs		Young & Thomas dephisgmator, 8 sections.	g & Tho hlegmato sections.		Rod and disc still-head 20 discs (with constrictions).	and disc ll-head ses (with rictions).	Pear still-head, 13 bulbs.	l-head, lbs.	Evap	Evaporator still-head, 5 sections.	il-head,	Young and Thomas dephlegmator, 18 sections.	oung and Thom dephiegmator, 18 sections.	nas
Vertical height from bottom to side tube in cm.		8	-		\$	- =	-	\$1\$	<u> </u>	63		62			75			130	
Weight of mixture distilled	004	99	2	904	28	22	007	8	ង	92	ន	99	23	100	50	25	400	100	2
Temperature range.	ı							P	Percentage	re weight	ď	distillate.	_						
80.2— 81.2	1	_	1	1	ı	-	1	1	1	1	1	1	1	8.5	6-2	6.5	32.7	\$2.4	81.5
81.2 83.5			9.0	9.0	0.0	70	8.0 8.0 8.0 8.0 8.0 8.0 8.0 8.0 8.0 8.0	9 9	9.9	9	57 5	0.8	မှ	24.0	50 c	77 ; 73 ;	10.4	9 6	٠. د د
83.2 86.3 86.3- 89.4			20.51	12.5	12.9	12.5	13.9	14.3	5 52 52 53 54 54 54 54 54 54 54 54 54 54 54 54 54	14.4	12.5	7.97	9 90 9 90 9 90	4 9	0 4 8 8	7 5 5 8 5 5 8 5 7	 	5 5	-0-
89.4— 92.5			œ %	6.4	4 00 9 00	2.5	10.4	9 9	9 9	9.9	9.6	80 0	8.6	64 ×	5 c	5. 5	6.5	Ģ1 9	8 9
95.6- 98.7			9	3.1	- 4, 5 60	0.9	4 6	÷	φ	9 90	9 90	9 64	8 63	9 59	9.1	4 64		9 90	9
88.7—101-8			4.0	44 c	4 4	20 A	80.0	0.4	8.9	4.6	7.0	4.0	900	:::	91	9.5	25	2:	6 9
104.8—107.9			. S	4 4	9 49	9 0	မှ တ မှ ထ	, ca	9.9	4 4	0 4	9.00	2 00 0 00	2.4	- 69	2 4°	7.0	: ±	5.0
107-9-110-3	- 6 - 6 - 6 - 6 - 6 - 6 - 6 - 6 - 6 - 6	18.7 2.5	-2.1	9 9	00 ec	~9 .8	8:3 10:5	. œ	-1 0	4.6	10.6 6.0	5.0 11.0	10 d	4 00 io 04	10.8		3.7	9 0	8.I 8.I
110.9 (by difference)	ष्ट्रो	갂	ı-	2.97	$\overline{}$	z-	17.1	15.0	16.0	18.4	18.6	81.6	21.0	80.8	28.4	83-0	43.9	-	84.7
	100.0	100-0	0.001	0.001	100.0	100.0	100.0	100.0	100.0	0.00	0.001	0.001	100-0	100.0	0.001	100-0	100-0	100.0	0.001
Weight of vapour and liquid in still-head.		90 64			28.9			5.8		č1	5.5	23	ç		2.0			12.1	
Percentage weight of distillate collected up to 95.6°.	8.65	9.6	44.4	52-0	2.09	46.4	4.64	2.63	48.0	51.8	8-64	51-2	1.07	8.67	6.87	46.6	8.63	48.6	47.9
Highest temperature reached.	110-0-11	110.55 107-9*		110-9-	barely 110-9°	107-65	.6-011	110-9-	barely 110-9	110-9	110-9	110.9°	110.0	110-9	110-9°	110-9*	110-9	110-9	110-9
Boiling point of residue.	110-9	109-25' 1 to 110-9° 1	110.7	.6-011	110°8° to 110°8°	106·0° to 110·9°	110-9	.6-011	110.7° 10.9°	110-9	110-9	110.0	.0.0II	110-90	110-9°	110-9	110-9°	110-9	110-0
Reference number.	XXIIIX	TILXXIV	XXV	XXVI	кхип	кжупп	XIXX	XXX	XXX	XXXII	XXXIII	XXXIV	XXX	XXXVI	XXXVII	XXVI XXVII XXVII XXIX XXX XXXI XXXII XXXIII XXXIV XXXV XXXVI XXXVII XXXII XXXIX	XXXXIX	Xr	XLI

* Then fell again to 107.4' as the last few drops came over.

† The Young and Thomas dephlegmator with 3 sections was unnecessarily long.

suitability of the dephlegmators for the distillation of small quantities of liquid. In this case, and also when 25 grams were distilled, XXV, XXVIII, and XXXI, the distillation was continued until there was no more liquid in the flask. After cooling, the liquid that flowed back into the flask, together with any that remained in the still-head, was distilled from a small bulb, and the boiling point noted, in order to find whether any benzene was still present.

It will be seen that, with 50 grams of the mixture, the Glinsky tube is far inferior to the others, no pure toluene being obtained. It will also be noticed that the residue, dried with phosphoric oxide, began to boil at a considerably lower temperature, 109.25°, than the final temperature registered by the thermometer when the distillation with the fractionating tube was stopped. This is an important point, which will be referred to later.

The separation of benzene with the Le Bel-Henninger still-head was not quite so good as with the Young and Thomas; that of toluene was distinctly worse, for the temperature barely reached 110.9° when the flask was quite empty; also, the boiling point of the residue was not quite constant (110.8—110.9°). With the Young and Thomas apparatus, 7.8 per cent. of pure toluene was collected before the flask was empty, and the residue boiled quite constantly at 110.9°.

The inferiority of both the Glinsky and the Le Bel-Henninger tubes, when small quantities of liquid are distilled, is far more marked with 25 grams of the mixture than with 50. With the Young and Thomas dephlegmator, the separation of toluene was certainly less satisfactory than when 50 or 400 grams of the mixture were distilled, for the temperature barely reached 110.9° at the end of the distillation, and the residual toluene was not quite pure (b. p. 110.7° to 110.9°). The results obtained are, in fact, very similar to those given by the Le Bel-Henninger tube with 50 grams of the mixture.

With the Glinsky and the Le Bel-Henninger tubes, the separation of benzene was not so good as with the Young and Thomas tube, but the inferiority is more obvious with the toluene, for in neither case was 108° reached at the end of the distillation. Also, the residues, especially with the Glinsky tube, contained considerably more benzene than the last drops of distillate, for, when distilled from an ordinary bulb, they began to boil at 102.5° and 106.0° respectively.

Another point of interest is that the percentage weight of distillate collected below 95.6° was decidedly lower with 25 grams of the mixture than with the larger quantities; indeed, with the Glinsky tube, the percentage, 44.4, was even lower than with the worst of the plain vertical still-heads.

For convenience of comparison, the results of the distillation of 50 and 25 grams of the mixture with the "rod and disc" and the "pear"

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still-heads, and of 100, 50, and 25 grams with the "evaporator" still-head with 5 sections, and also of 400, 100, and 50 grams with the Young and Thomas dephlegmator with 18 sections are given in the table. It will be seen that large quantities of pure toluene were obtained on distilling 25 grams of the mixture with the "rod and disc," "pear," and "evaporator" still-heads. The separation was, indeed, very nearly as good with 25 grams as with the larger quantities. It seemed useless to distil 25 grams of the mixture with the dephlegmator having 18 constrictions, because the weight of vapour and liquid in the still-head and still would be greater than the weight of toluene taken. With 50 grams of the mixture, however, the yield of pure toluene, though less than with the larger quantities, was still very good.

GENERAL REMARKS ON THE CONSTRUCTION OF DEPHLEGMATORS.

The results which have been described indicate the requirements which should be fulfilled in the construction of a dephlegmator in order that the best results may be obtained.

- 1. Ease of Construction.—I cannot, of course, speak for professional glassblowers, but I should find it more difficult to make a Glinsky or Le Bel-Henninger than a Young and Thomas dephlegmator.
- 2. Possibility of largely increasing the number of Sections.—As the efficiency of a dephlegmator or still-head increases with the number of sections (see 9, page 708), it is clearly a great advantage if the number can be increased without adding seriously to the difficulty of contruction. It has been pointed out (p. 701) that it is almost as easy to make a Young and Thomas dephlegmator with 12 or 18 constrictions as one with 2 or 3.
- 3. Convenience of Handling.—The reflux tubes, being inside the main tube in the Young and Thomas dephlegmator, are much better protected from breakage, and the apparatus is almost as convenient to handle as a plain straight tube.
- 4. Size of Constrictions, &c.—In the various forms of dephlegmator, the return flow of condensed liquid through the main tube is retarded at different levels by constrictions in the tube, assisted by glass bulbs, platinum gauze cones, or other obstructions. Now, as the amount of liquid flowing back at any level is greatest at the bottom of the tube and least at the top, it follows that, in order to retard the flow sufficiently to form a pool of liquid for the vapour to rise through, more complete obstruction is required at the top of the tube than at the bottom.

In the Le Bel-Henninger tube, however, the constrictions are usually made widest, and the platinum cones largest at the top of the tube. There is thus a tendency, on the one hand, for the liquid to flow past the

upper cones without collecting into a pool, and, on the other hand, for the quantity of liquid in the pools in the lower bulbs to be unnecessarily large.

A so-called 6-bulb Le Bel-Henninger tube, which I purchased from one of the best-known London dealers, failed in both respects. Moreover, only 5 cones were provided, although there were 6 bulbs and 6 reflux tubes; if, therefore, the apparatus had otherwise worked well, there could have been only 5 pools, and the condensed liquid in one of the reflux tubes (the lowest) would have remained practically stagnant throughout the distillation (see 6, below).

In the Young and Thomas apparatus, it is advisable to make the upper constrictions somewhat deeper than is shown in the diagram (Fig. 6b). The upper projection on the reflux tube may, in fact, be nearly as wide as the constricted tube. If the number of sections is large, the lower constrictions need be no deeper than that shown.

5. Width of Reflux Tubes and Depth of Traps.—It has been pointed out (p. 681) that, consistently with efficiency, the amount of condensed liquid in the still-head during distillation should be as small as possible. The reflux tubes should, therefore, not be made wider (in the part that is filled with liquid during the distillation) than is necessary to freely carry back the condensed liquid; also, the U-shaped parts, acting as traps, should be no deeper than is required to prevent the ascending vapour from forcing its way through them. Additional width or depth simply means waste liquid in the still-head.

If the number of sections is very large, the lower traps should be made rather wider than the upper ones.

On the other hand, the upper part of the reflux tubes may be advantageously made fairly wide so as to facilitate the entrance of condensed liquid and also to prevent bubbles or columns of vapour being caught and carried down with the liquid through the traps. Such columns of vapour, when formed, are liable to empty the traps of liquid and the ascending vapour may then pass more easily through the traps than through the pools of liquid formed by the obstructions.

On referring to Table IV (p. 702), it will be seen that the amount of vapour and condensed liquid in the still-head is much greater with the Le Bel-Henninger dephlegmator than with the other two. The poor results obtained with this dephlegmator at the highest temperatures on distilling 25 grams of the mixture were, I believe, largely due to this cause.

6. Flow of Liquid through the Reflux Tubes.—It is of the utmost importance that there should be a rapid flow of condensed liquid through the reflux tubes, especially if they are outside the main tube and are not heated by the ascending vapour. To take an extreme case, suppose that there is no back flow at all through the reflux tubes and that the

traps simply become filled with the first portions of condensed liquid. This lowest boiling liquid will thus remain lodged in the traps until the end of the distillation, and will then form part of the residue. In the distillation, for instance, of a mixture of benzene and toluene, the last fraction might consist of pure toluene, whilst the residue at the end of the distillation would be very rich in benzene.

Of the three dephlegmators compared, the Young and Thomas apparatus is the best in this respect; it possesses, also, the advantage that the reflux tubes are heated by the ascending vapour.

In the Glinsky apparatus, on the other hand, the flow of liquid was exceedingly slow, and it has been seen that, on distilling 50 grams of the mixture, and to a far greater extent on distilling 25 grams, not only was the separation of toluene—and even of benzene—worse than with the Le Bel-Henninger, although the amount of liquid in the still-head was much smaller, but also the residue was much richer in benzene than the last portions of the distillate.

With the Le Bel-Henninger tube, on distilling 25 grams of the mixture, the residue was also distinctly richer in benzene than the last portion of the distillate, but the difference was not nearly so marked as with the Glinsky tube.

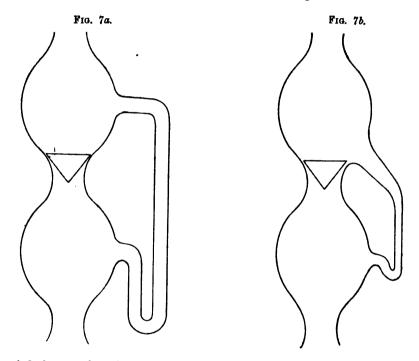
The larger the amount of liquid distilled, the less noticeable will be the bad effect of a slow flow though the reflux tubes; thus, on distilling 400 grams of the mixture, the results with the Glinsky tube were not greatly inferior to the others, but the inferiority became more and more marked as the quantity of liquid distilled diminished.

In fractionating tubes of the Glinsky or Le Bel-Henninger type, the upper end of the reflux tube should be wide and the junction with the bulb should be very low down. In this way, the quantity of liquid in the pool will be prevented from becoming unnecessarily large, and, also, more of the liquid will return through the reflux tube and less will find its way back past the obstruction. Figs. 7a and 7b (p. 707) will perhaps make these points clearer. Fig. 7a represents a form—not an unusual one—which is wrong, Fig. 7b one which is right, in principle.

7. Arrangement of the Reflux Tubes.—To get the best results, there should be a reflux tube connecting each bulb with the one below it, so that the change in composition may be regular from top to bottom of the dephlegmator. That is the case with the Le Bel-Henninger and the Young and Thomas dephlegmators, but in the Glinsky apparatus there is only one reflux tube connecting the top bulb practically with the still. Thus the condensed liquid which is returned to the still through the reflux tube is richer in the more volatile component of the mixture than the liquid in the pools.

8. Return of Liquid from Still-head to Still after the Distillation is stopped.—When the residual liquid is valuable, it is a great advantage that it should return as completely as possible from the still-head to the still. The weights of liquid actually left in the still-heads after cooling were as follows: Glinsky, 0.2 gram; Le Bel-Henninger, 1.4 grams; Young and Thomas, 0.55 gram. In this respect, and this only, the Glinsky dephlegmator gave the best results, but the amounts of liquid left in the "rod and disc," the "pear," and the "evaporator" still-heads were even smaller.

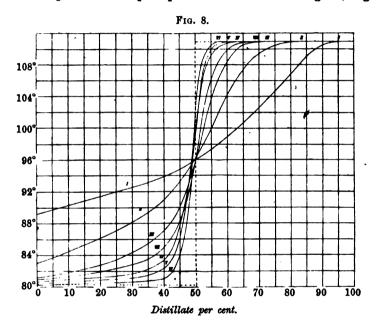
From what has been said, it will, I think, be gathered that the



inferior results obtained with the Glinsky and Le Bel-Henninger dephlegmators in the distillation of small quantities are partly due to the fact that the particular tubes employed possessed some of the faults indicated in Fig. 7a. Even, however, if these faults had been eliminated as completely as possible, and if the tubes had been of the same length, there can, I think, be no doubt that the Young and Thomas apparatus would still have given the best results, and the Glinsky by far the worst. The "rod and disc" and the "pear" and especially the "evaporator" still-heads can, however, be used for much smaller quantities than any of the dephlegmators.

9. Effect of increasing the number of Sections.—In order to find what improvement is effected by increasing the number of sections, distillations of 100 grams of the mixture were carried out with Young and Thomas dephlegmators with 3, 6, 12, and 18 sections. Finally, to see how complete a separation could be effected with the dephlegmator with 18 sections, a similar distillation was carried out at the rate of 30 instead of 60 drops a minute. The results are given in Table V, and for the sake of comparison the results of the distillation with the short plain still-head are added.

The improvement is perhaps better seen in the diagram, Fig. 8,



where the total weights of distillate are plotted against the temperature. In this diagram, curves are also given for the distillation with the "evaporator" still-head with 5 sections as well as with the short plain still-head. The dotted line shows the form that the curves would take if the separation were absolutely perfect.

	_						
Curve	I.	Short still-head.			Rate	60 dr	ops per minute.
,,	II.	Dephlegmator,	3 s	ections.	,,	60	37
,,	III.	,,	6	,,	,,	60	,,
,,	IV.	22	12	,,	"	60	,,
,,	₹.	**	18	,,	>>	60	,,
,,	VI.	,,	18	,,	,,	30	,,
,,	VII.	Evaporator still-head	l, 5	"	"	60	"

TABLE V.

			<u>.</u>			
Nature of still-head.	Short plain vertical tube.	Yo	ung and '	Thomas d	ephlegma	tor.
Number of drops of distil- late per minute.	60	60	60	60	60	30
Number of actions in de- phlegmator.	_	8	. 6	12	18	18
Vertical height from bot- tom to side tube in cm.	12	51	78	122	130	130
Temperature range.		Percer	itage weig	ght of dis	tillate.	
80·2°— 80·7° 80·7 — 81·2 81·2 — 83·2 81·2 — 86·3 86·3 — 89·4 89·4 — 92·5 92·5 — 95·6 95·6 — 98·7 98·7 — 101·8 101·8 — 104·8 104·8 — 107·9 107·9 — f10·3 110·9 (by difference)	2·1 28·4 18·0 10·9 8·6 7·2 7·2 6·8 5·9 4·9		0·6 22·8 14·5 6·3 8·1 2·5 2·1 1·7 2·0 3·9 4·6 8·0 27·9	3 21·1 18·6 4·3 1·9 1·8 1·3 0·8 1·0 1·8 4·1 5·5 87·0	\$ 82.4 9.6 8.0 1.5 1.2 0.9 0.8 1.0 1.1 1.4 2.8 6.0 38.3 100.0	33·7 7·2 3·4 2·0 1·2 0·9 0·7 0·3 0·4 0·6 1·2 2·8 3·0 42·6
Weight of vapour and liquid in still-head.	0.8	2.8	5.8	10.8	12.1	12·1
Percentage weight of distillate collected up to 95.6°.	48.5	48.9	49.8	49.0	48.6	49.1
Reference number.	XLII	XLIII	XLIV	XLV	XLVI	XLVII

^{*} Mean percentage calculated from values with 400, 50, and 25 grams.

In conclusion, I would say that, when only a moderate degree of efficiency is required, comparable with that of the ordinary 3-bulb Glinsky or Le Bel-Henninger dephlegmators, I would recommend either a "rod and disc" or a "pear" still-head of about the size VOL. LXXV.

described in this paper, in preference to either of them, or, indeed, to the Young and Thomas dephlegmator, on the grounds (1) that they are simpler, (2) that they are better suited for the distillation of small quantities, (3) that after the distillation is stopped the liquid returns almost completely from the still-head to the still. Of the two, I would prefer the "pear" still-head. A "rod and disc" or "pear" still-head of efficiency equal to that of the 12 or 18 column Young and Thomas dephlegmator would, however, be of altogether excessive length; therefore, if great efficiency is required, I would recommend either a Young and Thomas dephlegmator or an "evaporator" still-head. Of the two, the "evaporator" is superior, inasmuch as the amount of liquid in the still-head is considerably less, and also, after the distillation is over, the liquid in the still-head returns almost completely to the still.

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LXVI.—The Salts of Dimethylpyrone, and the Quadrivalence of Oxygen.

By J. N. Collie, Ph.D., F.R.S., and Thomas Tickle, Salters' Company's Research Fellow in the Research Laboratory of the Pharmaceutical Society of Great Britain.

Some years ago, one of us (Trans., 1891, 59, 617) noticed that when dehydracetic acid was boiled with fuming hydrochloric acid, a crystal-line compound containing hydrogen chloride was obtained. This substance at the time was considered to be a compound of diacetylacetone, as it was formed from the acid by addition of water and subsequent elimination of carbon dioxide:

$$C_8H_8O_4 + H_2O + HCl = C_7H_{11}O_8Cl + CO_2.$$

Feist(Ber., 1892, 25, 1067) pointed out later, however, that when fully dried over sulphuric acid this compound has the formula $C_7H_9O_2Cl$; still he also suggested that it was a derivative of diacetylacetone:

CH₃·CO·CH₂·CO·CH₂·CO·CH₃, diacetylacetone. CH₃·CCI:CH·CO·CH₂·CO·CH₃, compound (m. p. 154°).

The properties of the substance, however, are somewhat anomalous. It does not give a red coloration with ferric chloride, a reaction which is very characteristic of diacetylacetone; moreover, when dissolved in water, it reacts exactly as if it were a mixture of dimethylpyrone and hydrogen chloride. That a compound having the formula suggested

by Feist, with chlorine directly bound to a carbon atom, should be so easily decomposed by dissolution in water seemed unlikely, and for this as well as other reasons, we thought it worth while to investigate the substance further. It was therefore prepared from dehydracetic acid in considerable quantity, and recrystallised from dilute hydrochloric acid, from which it separated in transparent plates melting at 84—85°.

In aqueous solution, the compound is strongly acid, and the amount of hydrochloric acid present can be determined by titration with alkali of known strength. As already pointed out, the solution probably does not contain diacetylacetone, and this observation is further confirmed by the fact that barium hydroxide solution gives no yellow precipitate when added in excess. Moreover, the aqueous solution, when shaken with chloroform, yields dimethylpyrone, and, like a solution of this substance, is decolorised by bromine water, a milkiness being produced owing to the separation of one of the bromacetones.

The statement in the former paper (loc. cit., 620), that dimethylpyrone did not combine with hydrogen chloride, has been found to be incorrect, for both diacetylacetone and dimethylpyrone yield this additive product when allowed to evaporate with excess of hydrochloric acid. The substance has already been analysed by one of the authors, and partly by Feist, but further analyses were thought necessary to determine whether the hydrogen chloride was combined in the same manner as water of crystallisation, and whether the compound was one of constant composition. When dried in the air, it gave the following numbers on analysis, the water being determined by leaving the substance in a desiccator over sulphuric acid:

Found, HCl = 18.4; $H_2O = 18.3$. $C_7H_8O_{27}HCl + 2H_2O$ requires HCl = 18.5; $H_2O = 18.3$ per cent.

The salt was not changed in composition by recrystallising four times from water, but when it was left for some days slight decomposition occurred, and the amount of hydrochloric acid fell to 18·1, and finally to 17·9, per cent. In the same manner, the salt, when left in a desiccator for a month, lost a little more than the theoretical amount of water (loss = $20\cdot1$; $2H_2O = 18\cdot3$ per cent.), and the amount of hydrochloric acid in the dried salt was found to be proportionately low:

Found HCl = 20.8. $C_7H_8O_{27}HCl$ requires HCl = 22.1 per cent.

The dehydrated salt has been described by Feist. It is very hygroscopic; if left in the air, it rapidly absorbs water, passing first into the monohydrated salt (loc. cit., 619), and after a considerable time finally returns to the fully hydrated condition.

From these results, it appears that this curious compound behaves

much as an easily dissociated salt of a strong acid and a feeble base might be expected to do, and that the basic substance is dimethylpyrone. As it seemed somewhat remarkable that dimethylpyrone should possess such properties, a series of experiments was made in the hope that other salts than the hydrochloride might be isolated. Preliminary experiments soon showed that dimethylpyrone formed crystalline compounds with several other acids. The method employed when the acids, such as nitric or hydrobromic acids, were volatile, was to add an excess of the acid to the dimethylpyrone in an evaporating basin and allow the solution to evaporate in a vacuum over solid caustic soda; the crystalline separation was then collected and also dried in a vacuum over caustic soda. By this method, the hydrobromide, hydriodide, and nitrate were prepared. The other salts examined were the oxalate, tartrate, salicylate, chloracetate, picrate, and platinochloride. Several attempts to prepare the acetate and the sulphate were made, but without success.

Dimethylpyrone Hydrobromids, C₇H₈O₂, HBr, was prepared by evaporating a solution of dimethylpyrone in fuming hydrobromic acid in a vacuum over solid caustic soda. It crystallises in thin, transparent, slightly deliquescent plates, which were dried on a porous tile and left in a vacuum over caustic soda. The hydrogen bromide present was estimated by titration of the aqueous solution with decinormal soda and also with decinormal silver nitrate.

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Found, HBr = 39.4; Br = 39.0.

C_7H_8O_{99}HBr requires HBr = 39.5; Br = 39.0 per cent.
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Dimethylpyrone Hydriodide, C₇H₈O₂,HI, formed in a manner exactly similar to that employed in the preparation of the hydrobromide, crystallises in long needles and decomposes somewhat in air into iodine and other substances. When freshly prepared, quickly dried on porous porcelain, and then in a vacuum over caustic soda, it gave the following result, when titrated with decinormal silver nitrate:

Found,
$$I = 51.5$$
. $C_7H_8O_{29}HI$ requires $I = 50.8$ per cent.

Dimethylpyrone Platinochloride, $(C_7H_8O_2)_2$, H_2PtCl_6 .—When moderately strong solutions of dimethylpyrone hydrochloride and platinic chloride are added to one another, a copious precipitate of this salt is at once obtained, and its formation and appearance forcibly recall the action of platinic chloride on the hydrochlorides of bases such as those of the pyridine series. The platinochloride was recrystallised from water, and after drying did not lose weight when left for a considerable time in a vacuum desiccator.

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Found, Pt = 29.4 and 29.5. C = 26.1; H = 3.0. (C_7H_8O_2)_2H_2PtCl_6 requires Pt = 29.6; C = 25.5; H = 2.7 per cent,
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Dimethylpyrone Nitrate, C₇H₈O₂,HNO₃, crystallises from a strong solution of dimethylpyrone in fuming nitric acid in well-shaped, rhombic plates, and when pure seems to be perfectly stable in air. When dissolved in water, it forms a strongly acid solution, and was analysed by titrating with soda.

Found, $HNO_8 = 33.9$. $C_7H_8O_9$, HNO_3 requires $HNO_3 = 33.7$ per cent.

Dimethylpyrone Oxalate, $(C_7H_8O_2)_2$, $H_2C_2O_4$.—The examination of this salt seemed to present several points of interest, because oxalic acid is an organic acid, and, being dibasic, might form an acid and a normal salt. Accordingly, a series of experiments were made with varying quantities of dimethylpyrone and oxalic acid.

- (1) When a large excess of oxalic acid is added to a solution of dimethylpyrone, nearly pure oxalic acid crystallises from the solution, and this is also the case when three parts of oxalic acid and two parts of dimethylpyrone are employed, but on further evaporation a salt separates containing 42·2 per cent. of anhydrous oxalic acid ($C_7H_8O_2,H_2C_2O_4$ requires 42·0 per cent.). This compound, however, is not stable, for on recrystallisation, or on mixing together equal parts of dimethylpyrone and oxalic acid, crystals containing 45·5 per cent. and then 33·5 per cent. of oxalic acid separate from the solution.
- (2) When a solution containing dimethylpyrone, either in large excess or in the proportion of two to one of oxalic acid, is allowed to crystallise, the normal salt separates from the solution. Several analyses of the amount of acid in different preparations were made: Found, 26.4, 26.1, 26.2 per cent. A sample was also recrystallised from water four times, and each crop of crystals analysed, with the following results:

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Oxalic acid.—(1) 26.6; (2) 26.4; (3) 26.4; (4) 26.4. (C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>)<sub>2</sub>,H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> requires 26.6 per cent. of oxalic acid.
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The melting point of dimethylpyrone oxalate is 121—122°.

Dimethylpyrone Tartrate.—When dimethylpyrone and tartaric acid, in molecular proportion, are mixed and allowed to evaporate in a vacuum desiccator, circular groups of needle-shaped crystals radiating from a common centre separated when the solution was of the consistence of a syrup; these were broken up and dried on a porous tile. The salt is not deliquescent.

Found, tartaric acid = 59.2.

C₇H₈O₂,C₄H₆O₆ requires 54.7 per cent. of tartaric acid.

On recrystallisation from water, the salt that eventually separated by evaporation in a vacuum desiccator gave, after leaving in a vacuum until dry, 38.5 per cent. of tartaric acid, $(C_7H_8O_2)_2C_4H_6O_6$ requiring

37.7 per cent. This salt, therefore, is probably similar to the oxalate in constitution.

Dimethylpyrons Chloracetate, C₇H₈O₂,C₂H₈ClO₂.—When dimethylpyrone and chloracetic acid, in molecular proportion, are left over solid caustic soda in a vacuum, the solution deposits a mass of needleshaped crystals; these were dried on a porous tile and then in a vacuum desiccator and analysed.

Found, chloracetic acid = 43.5.

C₇H₈O₂,C₂H₃ClO₂ requires 43.3 per cent. of chloracetic acid.

Dimethylpyrone Salicylate was formed when nearly equal weights of salicylic acid and dimethylpyrone were dissolved in boiling water and, on cooling, separated as an oil which eventually crystallised.

Dimethylpyrone Picrate, C₇H₈O₂,C₆H₂(NO₂)₃OH.—Dimethylpyrone and picric acid, in molecular proportion, were dissolved in hot water, and, on cooling, a well crystallised salt separated which melted at 101—102°. It was recrystallised from water, and as the melting point remained constant it was analysed. When pure, it forms yellow, acicular crystals very similar in appearance to picric acid.

Found, nitrogen = 11.9 per cent.

$$C_7H_8O_2$$
, $C_6H_2(NO_2)_8OH$ requires $N = 11.9$ per cent.

All attempts to prepare the acetate and the sulphate were unsuccessful. When a solution of dimethylpyrone in acetic acid is evaporated, only the former remains; also, when it is mixed in the proper molecular proportion with sulphuric acid, an uncrystallisable syrup results.

That dimethylpyrone can form a series of salts such as we have enumerated seems to be of very great interest. The definite nature of the substances is proved by the method of preparation, and by the fact that such salts as the hydrochloride are practically unchanged when dried over caustic soda in a vacuum. Ordinary graphic formulæ fail to account for the existence of such substances; a formula such as that already given for the hydrochloride or either of the following,

does not explain the formation of dimethylpyrone and hydrochloric acid when the hydrochloride is dissolved in water, still less can formulæ based upon these types be given for the other salts. More-

over, chlorine compounds having these formulæ would not be expected to give platinochlorides. There is, however, an alternative. If we regard these compounds as salts of a feeble base with strong acids, a possible solution of the difficulty is reached. Moreover, there is a close resemblance between these products and those formed by dimethylpyridone:

Dimethylpyridene hydrochloride.

Dimethylpyrone hydrochloride.

This, however, involves an assumption that oxygen is quadrivalent, but there are many compounds that support this view: methylic ether hydrochloride, ethylic ether hydriodide, ethyl peroxide, acetyl peroxide, and several others:

The numerous peroxidised compounds obtained by Nef may also be cited (Annalen, 1897, 298, 292), and in addition to these, Brühl has lately drawn attention to the fact that the observed refraction in the case of hydrogen peroxide is much greater than that calculated, and advocates the quadrivalence of oxygen in that compound and also in water (Ber., 1897, 30, 160). J. F. Heyes (Phil. Mag., 1888, [v], 25, 221) has also advocated the quadrivalence of oxygen in order to explain, among other points, the difference between such peroxides as MnO_2 and BaO_2 on the one hand, and CO_2 , SnO_2 , &c., on the other, and Meldola (ibid., 26, 403) has suggested that the oxygen atom in the azo- β -naphthols may be quadrivalent. The anomalous behaviour of an aqueous solution of ethylene oxide also suggests that it may contain a hydrate of the following composition:

for how else can the precipitation of metals as hydrates from their salts by ethylene oxide be explained?

It is noteworthy, too, in this connection, that oxygen in the periodic arrangement of the elements finds its place near nitrogen. phosphorus, sulphur, and the halogens, all of these elements exhibiting dual valency.

Necessarily, the tendency for oxygen to form definite compounds in which its higher valency is evident can at best be but feeble, and if such be the fact it will only be in favoured cases that isolation of the compound can be effected. The combination of one oxygen and five carbon atoms in a ring seems to be one of these. A. G. Perkin (Trans., 1896, 69, 439) has already noticed a very large number of acid compounds of natural yellow colouring matters, and the phthaleins seem to form similar derivatives (Baever, Annalen, 1876, 183, 1; Fischer, Annalen, 1876, 183, 63; Nietzki and Schröter, Ber., 1895, 28, 50). An interesting point about the compounds to which A. G. Perkin calls attention is the fact that many of them are coloured, for if, as some chemists believe, colour in a compound is indicative of quinonoid structure in the molecule, then possibly the grouping indicated in formula I may be present in these substances Now from dimethylpyrone, chelidonic acid, meconic acid, and similar compounds, coloured derivatives are easily obtained. Dimethylpyrone itself gives a canary yellow barium salt with baryta water on warming; Feist, who discovered this compound, gave it the formula II, but if oxygen can behave as a quadrivalent element, then it is possible to represent the substance as possessing a quinonoid structure (III):

III. Quinonoid formula.

and possibly the yellow salts of meconic and xanthochelidonic acids owe their colour to a similar molecular grouping.

The question whether oxygen possesses this residual affinity or not is one of the very greatest interest, for if it is allowed that the oxygen atom can show, even feebly, a valency greater than two, then a new light is thrown on the reactivity of all oxygen compounds. It seems inconceivable that any reaction can take place between two molecules unless they are brought into molecular contact, and actual chemical union of the molecules is the most obvious way in which this might be expected to occur. Nearly all organic oxygen compounds react easily with acids and alkalis; perhaps their peculiar chemical activity may be due to this residual affinity of the oxygen atom, and alcohol, which is usually regarded as a saturated

may react with such agents as mydriodic acid in the following manner:

IE:

Innumerable instances might of course be given of compounds and reactions that receive additional explanation by this hypothesis: oxidation and reduction by hydrogen peroxide, the formation either of ortho- and para- or of meta-substituted derivatives from oxygenated benzene compounds, etherification, hydrolysis, and many more.

Moreover, if oxygen can replace phosphorus, nitrogen, or sulphur in bases, then these oxygen compounds can be viewed as derivatives of the hypothetical base, oxonium hydroxide, OH₂OH, just as the similar compounds of nitrogen, phosphorus, sulphur, and iodine are supposed to be derived from the hypothetical bases:

Dr. Kellas, of University College, has kindly determined the electrical conductivities of dimethylpyrone hydrochloride and oxalate in aqueous solution.

Volume of solu- tion containing	Мо	lecular or equivale	nt conductivit	ies.
equivalent quan- tities. Dilu- tion in litres.	Hydrochloric acid.	Hydrochloride.	Oxalate.	Oxalic acid.
2 4	358 366	217 269	104	
8	878	811	153	1
16	386	387		4
32	893	861 32	244	285
64	899	874	280	319
128	401	375	306	845
256	408	377	321	369
512	402	377	329	388
1024	403	876	331	408

These numbers, therefore, on comparison with those for hydrochloric and oxalic acids, seem to show clearly that dimethylpyrone hydrochloride and oxalate, when in aqueous solution, reach at high dilutions maxima of dissociation which are in both cases far below the numbers that should be obtained if complete dissociation had taken place.

RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

LXVII.—Chemical Examination of the Oleo-resin of Dacryodes Hexandra.

By Andrew More, A.R.C.S.

THE specimen of cleo-resin examined was obtained from trees growing on Pond Mountain, in the island of Montserrat, W.I. The resin was accompanied by some leaves of the tree from which it had been extracted, and these were submitted to the Director of Kew Gardens for identification. The plant was pronounced to be the 'mountain gommier,' or incense tree, *Dacryodes hexandra*, and it appears to be abundant throughout the West Indies. The cleo-resin is collected from the living trees, and is largely used for lacquer (see *Kew Bulletin*, 1891, 149).

The crude oleo-resin was a very sticky, white solid with a strong aromatic odour, and contained a few fragments of leaves and woody matter. It was first submitted to steam distillation, to separate the essential oil, and during the process, the resin melted sufficiently to form a layer above the water, but it was never very fluid. After all the oil had distilled over, the soft residual mass was removed from the flask and on cooling it solidified. The water which remained with the resin was evaporated to a small bulk, but nothing was left except a few tarry drops and a slight sticky residue.

The oil separated from the distillate amounted to 16 c.c. for every 100 grams of the oleo-resin employed, and I am indebted to Professor Tilden for its examination. After shaking with a saturated solution of sodium hydrogen sulphite, 60 c.c. of the oil were not reduced in volume, although the aqueous solution contained a trace of an aldehyde which reduced silver. The oil, washed with water, dried and distilled, gave a series of fractions from 156° to 180°, and a viscid, brown residue of higher boiling point which was too small in amount for further examination. Phenols were practically absent from the various fractions. The fractions of low boiling point, 156—163°, contained a large proportion of lavorotatory pinene, which was identified by its odour, boiling point, and by the preparation of the familiar monohydrochloride melting at 128°.

The fraction boiling at $173-176^{\circ}$ was saturated with dry hydrogen chloride; it gave a purple colour at first, which faded, and on cooling to about -10° the whole solidified, forming a nearly white, crystalline mass. After crystallisation from ether, this hydrochloride formed long, flat prisms melting at $.71^{\circ}$, and by its odour and melting point served to establish the presence of sylvestrens. The fraction of hydrocarbon from which this was obtained was strongly levorotatory, and

it would have been interesting, if possible, to separate the pure hydrocarbon for comparison with Atterberg's sylvestrene, which is dextrorotatory (*Ber.*, 1878, ii, 1206); the quantity of material was, however, far too small for this purpose.

Limonene was probably present in small quantity, but phellandrene, terpinene, and cineol could not be detected.

The estimated proportions of constituents of the oil were:

Pinene (lævorotatory)	64 pe	r cent.
Sylvestrene (lævorotatory)	17	,,
Other liquids, undetermined	6—7	,,
Resin and loss	12-13	••

The resinous mass left after steam distillation was reduced to coarse powder, and alcohol was added until the bulk was about doubled. After a few hours, the dark yellow liquid was drained off with the help of the suction pump, and a mass of very small, nearly white needles, mixed with particles of vegetable tissue, remained on the filter, the crude product from 500 grams weighing 109 grams. The solid was crystallised several times from boiling 80 per cent. alcohol (methylated spirit) until the melting point was constant.

The dark yellow filtrate, containing the part soluble in cold alcohol, left a soft varnish on evaporation. This substance has not been fully investigated, but it does not contain any appreciable quantity of ordinary resin acids.

The crystalline compound is deposited from all solvents in tufts of white needles and melts at 166—167°; 100 grams of absolute alcohol dissolve 5.935 grams, and 100 grams of benzene dissolve 7.810 grams at 16°; it is quite insoluble in water.

On combustion, the following percentages were obtained:

				Calcul	ted for
I.	II.	III.	Mean.	C22H26O.	C25H44O.
C83·61	83.58	83.10	$83 \cdot 43$	83.52	83.33
H11·49	11.69	11.32	11.50	11.42	$12 \cdot 22$
O (by difference	e)		5.07	5.06	4.44

The molecular weight of the substance was determined by the cryoscopic method with a Beckmann apparatus, the results being checked by determinations with pure naphthalene. Using benzene as the solvent, the values for the molecular weight were 366, 366, and 372, but with acetic acid as solvent the results were lower, namely, 312, 314, and 358, the mean being 368 in benzene and 328 in acetic acid. The value for $C_{22}H_{36}O$ is 316. It appears probable therefore that the molecular weight is greater than this, and the formula $C_{25}H_{44}O$, corresponding to the molecular weight 360, seems to be more nearly in conformity with experimental results.

The substance is slightly soluble in concentrated sulphuric acid, and is reprecipitated on the addition of water. Bromine, dissolved in petroleum, and added to a petroleum solution of the compound, is very slowly decolorised, colourless, solid globules being deposited; these probably consist of a brominated derivative, but the substance changes in a short time to a purplish mass, and is unsuitable for analysis. It could not be crystallised from any solvent, and the corresponding chlorine derivative, which is also uncrystallisable, could not be obtained pure. It is insoluble in aqueous potash, and showed no sign of hydrolysis when boiled with strong alcoholic potash for 8 hours, the original substance being recovered unchanged. Fusion with potash also produced no change until the temperature was raised above the melting point, when charring occurred.

Concentrated nitric acid, added to an acetic acid solution, gives a yellow colour; such a solution was heated for 12 hours with fuming nitric acid to complete the reaction, and, on the addition of water, a soft yellow, uncrystallisable substance was precipitated, which was not changed by further heating with the acid. The yellow substance contained nitrogen varying in amount between $10\cdot23-11\cdot10$ per cent.; this corresponds nearly to the formula $C_{25}H_{40}O(NO_2)_4$, which requires $N=10\cdot3$ per cent.

The substance being soluble in glacial acetic acid, an attempt was made to oxidise it by means of chromic acid. A yellowish precipitate was obtained, which was dissolved in dilute caustic soda solution, filtered, and reprecipitated with hydrochloric acid. The product was soluble in alcohol, benzene, petroleum, and chloroform, but was uncrystallisable; it began to melt at about 149°. It became very strongly electrified when powdered. The oxidation product seemed to possess feeble acid properties, as it dissolved in caustic alkalis, and gave precipitates with lead and barium salts, but the molecular weights deduced from analyses of these salts were not concordant, and the cryoscopic method was therefore used. Benzene being the solvent, a depression of the freezing point was observed corresponding to 812 for the molecular weight. On combustion, the following percentages of carbon and hydrogen were obtained:

C = 72.91 and 72.01; H = 8.65 and 8.90. $C_{50}H_{72}O_{10}$ requires C = 72.11; H = 8.65 per cent.

The molecular weight for $C_{50}H_{72}O_{10}$ is 832, and these results seem to indicate that, in the process of oxidation, two molecules of the substance are condensed into one.

An attempt was made to reduce the compound by heating in sealed tubes with phosphorus and concentrated hydriodic acid, but the product was a varnish-like substance which contained iodine. After treatment with zinc dust in acetic acid and removal of the iodine, it

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was still of the consistence of vaseline, which it closely resembled. Distillation with zinc dust gave a paraffin-like product, very similar to that which was obtained by reduction with hydriodic acid. The solid part of the distillate had a strong, greenish fluorescence, resembling that of commercial "petroleum jellies."

The remarkable indifference to the action of alkali and oxidising agents led at first to the idea that this compound must have the constitution of an ether, and not that of an ester or an alcohol. It was found, however, that on heating with acetic anhydride, a substance was produced which was evidently an acetyl derivative; this crystallises, not, like the original substance, in needles, but in small, lustrous scales, and melts at 199°. The percentage of acetyl was determined by boiling with alcoholic potash for half an hour, diluting with water, distilling off the alcohol, filtering, acidifying with sulphuric acid, and distilling off the acetic acid. The distillate was treated with excess of well-washed barium carbonate, and the barium acetate dried at 130°, the result being checked by conversion of the acetate into barium sulphate. On analysis:

0.9942 gave 0.2834 Ba $(C_2H_3O_2)_2$ and 0.2590 BaSO₄.

This corresponds to acetyl = 9.61; theory requires 10.69 per cent.

As the acetylation seemed incomplete, the process was repeated, the boiling being continued for $2\frac{1}{2}$ hours with excess of acetic anhydride; the product then melted at 200° , and contained 9.49 per cent. of acetyl. It was then heated in a sealed tube with acetyl chloride for 4 hours at 100° ; there was no pressure in the tube after cooling, and the product, which melted at 199.5° , contained 9.27 per cent. of acetyl.

There can be little doubt, therefore, that the substance under investigation is a monohydric alcohol, $C_{25}H_{43}$ ·OH, and that it is a saturated compound.

A substance obtained from birdlime has been described by Personne (Compt. rend., 1884, 98, 1586) under the name ilicic alcohol, which in properties approaches very nearly to the compound described in this paper, and is probably identical with it. As the mean of five analyses, it was found to contain carbon = 83·36, hydrogen = 12·20 per cent., and the formula assigned to it was $C_{25}H_{44}O$, which has also been adopted for the substance described in this paper. The melting point of the acetyl derivative is given by Personne as 204—206°.

Divers and Kawakita (Trans., 1888, 53, 274) have also isolated a similar alcohol from birdlime, but although in melting point and composition their compound agreed very closely with Personne's ilicic alcohol, they failed to obtain an acetate by treating it with acetic anhydride.

Cork is known to yield a crystalline compound, to which the name

cerin has been given. A specimen of cerin, prepared many years ago by Professor Tilden, was found to melt at 251°. It was unaltered by boiling with acetic anhydride, and was so slightly soluble in cold benzene that an attempt to determine its molecular weight by the freezing point method was only imperfectly successful. The number 355 was obtained, and this approximates to the value 374, calculated for the formula C₂₆H₄₆O, attributed by Divers and Kawakita (*loc. cit.*) to mochylic alcohol, which is also present in Japanese birdlime. Mochylic alcohol melts at 234°, and, like cerin, does not give an acetate. Combustion of this specimen of cerin, however, gave the following numbers, which show that it is not a substance of the same character:—

C = 79.32 and 79.22; H = 10.98 and 11.01 per cent.

Cerin was but slightly soluble in boiling alcohol, even with the addition of potash, by which it was unaffected; no acids could be detected in the solution, and the substance was recovered unchanged. Notwithstanding the large proportion of oxygen it contains, this specimen of cerin is therefore apparently neither an acid nor an ester.

This investigation has been carried out under the direction of Professor Tilden, whom I wish to thank for his valuable advice and assistance.

ROYAL COLLEGE OF SCIENCE, LONDON.

LXVIII.—Estimation of Boric Acid mainly by Physical Processes.

By A. WYNTER BLYTH.

For some time, the author has been investigating the behaviour of boric acid under various conditions, and finds that when 50 milligrams of pure boric acid are distilled with 50 c.c. of methylic alcohol, the greater portion of the boric acid is carried over in the first fifth of the distillate, whereas if water is employed, very little of the acid passes over in the first two-fifths, and the greater portion remains behind, even when the distillation is carried to dryness. The presence of substances, such as glycerol, mannitol, and tartaric acid, diminishes the volatility of boric acid in methylic alcohol solution.

Estimation of Boric Acid by its effect on the Rotation of a Solution of Tartaric Acid.

It has been long known that the addition of boric acid to tartaric acid, mannitol, or compounds of the mannitol group has the effect of

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remarkably increasing the rotation of these substances. No one, so far as the author is aware, has yet applied this property to the estimation of boric acid.

After numerous experiments in this direction, the following process was finally adopted: 3 grams of ordinary dextrotartaric acid were dissolved in a little methylic alcohol, and to this solution various quantities of boric acid were added, and the volume made up to exactly 20 c.c. at 18°; in every case therefore the amount of tartaric acid was constant. The solution was then examined by polarised light. The instrument used was a Laurent's half-shadow saccharimeter, the source of light being an ordinary electric glow-lamp behind finely ground glass; the results were checked by the sodium light, but no material differences were observed.

The following is the "specific rotation," using this expression arbitrarily, as the specific rotation has been calculated from the tartaric acid alone:—

Boric acid.	Rotation.	Boric acid.	Rotation.
0.00 per cent.	5·07°	2.0 per cent.	17·5°
0.05 ,,	9.0	2.5 ,,	19.0
1.0 ,,	13.2	3.0 ,,	20.0
1.5 "	15.5		

Solutions of boric acid under 1 per cent. should be examined in a 5 dcm. tube. This method of estimating boric acid is convenient and reliable, and its employment is facilitated if a table is constructed for the polarimeter for quantities from 0.02 to 4 per cent. and the results are plotted as a curve, since fractional parts can then be obtained by interpolation.

The boric acid can, of course, be recovered by distillation, no loss of substance occurring, save that which may be due to transfer from one vessel to another. Hence the polarimetric estimation need not be exclusively relied on, but may be employed to check other methods.

Estimation of Boric Acid by the Loss of Carbon Dioxide.

In all the text-books, it is asserted that, in order to estimate boric acid indirectly by the loss of carbon dioxide, the boric acid solution must be evaporated to dryness with the alkali carbonate, and then fused. I find, however, that when boric acid is simply boiled with sodium carbonate solution, constant results are obtained in accordance with the following equation:

$$Na_{2}CO_{2} + 4H_{2}BO_{3} = Na_{2}B_{4}O_{7} + CO_{2} + 6H_{2}O$$
;

0.177 milligram of carbon dioxide is evolved for every milligram of

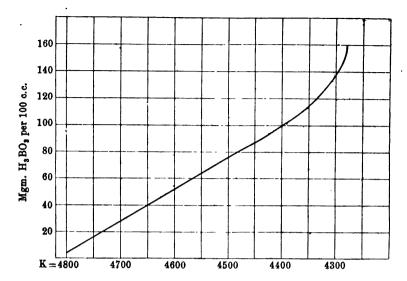
boric acid used, the mean of over 50 experiments with quantities of boric acid varying from 30 to 160 milligrams, being a loss of 0.2 milligram of carbon dioxide for each milligram of boric acid—an amount which is a little higher than the theoretical. An apparatus similar to that described in the Proceedings (1899, 15, 50) should be employed in these estimations.

Estimation of Boric Acid by Determining the Conductivity of the Solution.

The conductivity of a solution is an extremely delicate method of estimating the final reaction which takes place when a mineral acid is neutralised by an alkali, or vice verst. Experiments were made to ascertain whether this method could be applied to the estimation of boric acid; by careful working, it is possible to detect the successive replacements of hydrogen in a solution of boric acid, but, as might be expected, the process is tedious, requires a number of precautions, and the differences in the conductivity with successive increments of sodium carbonate are small. If, however, the same solution of sodium carbonate is employed, and known quantities of boric acid in solution are added, the mixture being boiled and then cooled to 18°, the increase in the resistance of the liquid is proportional to the boric acid present.

The results of the estimation of the conductivity are contained in the following table, and are illustrated graphically by the curve, $K = \overline{W}$, C being the resistance of the vessel as determined by experiments on solutions of known conductivity, W the resistance in ohms of the liquid under examination, and for the 0.3 per cent. sodium carbonate solution, K = 0.004789.

	e acid in 0 c.c.	•			K.
10	mgrms.(+	5 c.c. of 6 per	cent. sodium c	arbonate solut	ion) 0:00475
20	,,	,,	,,	**	0.00473
40	,,	,,	,,	,,	0.004650
50	,,	,,	,,	,,	0.004605
60	"	"	,,	,,	0.004565
70	"	,,	,,	"	0.004525
80	"	,,	,,	"	0.004483
90	,,	"	,,	,,	0.004435
100	"	,,	,,	,,	0.00400
110		,,	"	,,	0.004303
120		,,		,,	0.004320
	••	,,	"	••	



The estimation of boric acid by the conductivity method may be combined with that based on the loss of carbon dioxide, that is to say, 5 c.c. of 6 per cent. sodium carbonate solution may be boiled with various quantities of boric acid, the solution diluted to 100 c.c., the conductivity estimated at 18° by Kohlrausch's telephone method, and the same solution then used for the estimation of carbon dioxide, the one process checking the other.

LXIX.—The Blue Salt of Fehling's Solution and other Cuprotartrates.

By Orme Masson, M.A., D.Sc., and B. D. Steele, B.Sc.

Electrolytic Experiments.

In the course of the investigation by one of u of a new method for the direct comparison of ionic velocities (*Phil. Trans.*, 1899, 192, 331), it became desirable to ascertain whether the blue salt of Fehling's solution owes its colour to its positive, or, as seemed more likely, to its negative ions. In the experiment adopted to test this question, it was necessary to have the blue solution as free as possible from excess of alkali. It was therefore prepared in the following manner. Pure cupric tartrate was made by mixing solutions of cupric sulphate and Rochelle salt in the proper proportion, and washing the sparingly soluble, blue, crystalline precipitate ($CuC_4H_4O_6+3H_2O$). This was

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then mixed with a little water, and caustic potash solution was added slowly, with continual shaking, until almost, but not quite, the whole of the precipitate was dissolved. The clear, filtered liquid had the appearance of Fehling's solution, but was perfectly neutral to litmus. Two flasks, provided with side necks, were connected with each other by a straight, horizontal glass tube, 12 cm. long and of narrow bore, the ends of which were covered with short pieces of rubber tubing and thus made to fit tightly into the necks. Before making this connection, however, the tub was filled with a transparent jelly containing sodium chloride in the proportion of a normal solution and 12 per cent. of gelatine. Platinum electrodes were placed in the flasks, which were now filled with the deep blue neutral solution, and the electrodes were connected with a battery giving an E.M.F. of about 40 volts. The apparatus was placed in a bath of cold water, deep enough to cover the tube and reach to the shoulders of the flasks, in order to counteract the heating effects of the current. It soon became manifest that deep blue anions were travelling through the tube, and that the cathions of the solution (presumably K) were colourless. experiment was continued for some hours without affecting this The platinum cathode was then found to be plated with copper, which was undoubtedly due to secondary action of the discharged Na ions, for the blue ions had been visibly travelling away from the cathode all the time. The experiment is an easy one to carry out, and illustrates very prettily the theory of the formation of secondary products in electrolysis and its application to electro-plating.

A second experiment was then performed, in which the flasks containing the anode and the cathode were filled respectively with cupric sulphate solution and with the deep blue solution, the tube being filled with the jelly as before. Two blue boundaries were now seen to advance through the tube in opposite directions, a deep blue one moving from the cathode end, as in the first experiment, and a paler blue one moving towards it from the anode cell. Thus the contents of the tube became divided visibly into three parts-light blue cupric chloride jelly at the anode end, colourless sodium chloride jelly in the middle, and deep blue sodium-cuprotartrate jelly at the cathode end-of which the coloured parts were gradually increasing in length at the expense of the intermediate colourless one. The tube was graduated, and from experiments which are fully discussed in the paper already referred to, it was known that the visible boundaries should travel with velocities having a certain relative value (approximately 2:3), and should therefore meet at a certain point in the tube, provided that they were the only boundaries in the jelly, and that no invisible anions, except those of the chlorine of the original jelly, were travelling ahead of the dark blue enes. It soon was evident, however, that the expected ratio of velocities was not being maintained; and the cause of this was manifest when the light blue boundary, on reaching the calculated mark, while the dark blue boundary was still some way off, suddenly formed a pale blue precipitate as a septum across the tube. This proved that the dark blue solution contained, besides the coloured anions, some other, faster, colourless kind, which had the power of forming an insoluble cupric salt. The probability was that they were the ordinary tartaric ions; and, if so, the reaction between copper tartrate and caustic potash, by which the deep blue neutral solution was prepared, could not be so simple in its character as was at first assumed.*

Synthetical Experiments.

It was evident that further light might be thrown on the question of what occurs in this reaction by ascertaining the exact quantity of alkali required for the production of the neutral blue solution. The following experiments were therefore performed, using caustic soda as the alkali, and may be taken as confirmatory of Kahlenberg's statement (Zeit. physikal. Chem., 1895, 17, 590), that when caustic potash acts on copper tartrate, 63 per cent. of its equivalent (that is, CuC₄H₄O₆ takes 0.63 of 2KOH) is required to completely dissolve the salt and to develop an alkaline reaction. Kahlenberg, however, maintained that the blue salt is produced by interaction, in the proportion CuC₄H₄O₆: KOH, and represented its constitution by the formula

$$0 < \substack{\text{Cu+O+CO+CH(OH)+CH(OH)+COOK}} \cdot$$

It will be shown that this theory does not correctly represent the facts.

Precipitated copper tartrate was thoroughly washed and dried at 105°. At this temperature, it loses its water of crystallisation without further decomposition, as was proved by combustion:

0.5151 gave 0.4290
$$CO_2$$
 and 0.0999 H_2O . $C = 22.71$; $H = 1.96$. $CuC_4H_4O_6$ requires $C = 22.69$; $H = 1.90$ per cent.

Small quantities of this dry salt were then tested in stoppered flasks

* After the experiments described above had been performed and some further progress had been made with this investigation, the May (1898) number of the Journal was received containing an abstract of a paper in the Zeitschrift für Elektrochemie on Ionic Reactions, by F. W. Küster (Abstr., 1898, 74, ii, 205), in which the negative character of the blue ion of Fehling's solution is proved by an experiment similar in principle to ours. Küster's original paper is not obtainable in Melbourne. Earlier, but less direct, evidence of the same fact was given by Louis Kahlenberg (Zeit. physikal. Chem., 1895, 17, 586) in an important paper on complex tartrates.

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with N/2 caustic soda solution. In each case, the alkali was added in successive portions, and the flask was well shaken and then left after each addition in order to give the salt every chance of dissolving. As the end of the reaction (complete solution) was approached, the undissolved salt had a tendency to remain suspended in the deep blue liquid as a silky turbidity, which slowly settled down as a precipitate if more alkali were required, or equally slowly went into solution if enough had been added. This made it possible to hit the end point with fair accuracy, the resulting solutions being tested with litmus paper, which was then rinsed with water to remove the blue copper compound. The following results were obtained:

	Grams of CuC ₄ H ₄ O ₆ .	C.c. of N/2 NaOH.	Ratio, NaOH CuC4H4O6	Reaction to litmus.
A	1.470	$17 \cdot 12$	1.23	Neutral.
\mathbf{B}	1.149	13.65	1.26	Faint alk.
\mathbf{C}	1.238	14.63	1.25	Faint alk.
D	0.584	6.73	$1 \cdot 22$	Neutral.

A fifth experiment on a small scale was made by mixing copper sulphate and tartaric acid solutions, in molecular proportion, and running in sufficient caustic soda to first neutralise the acid and then dissolve the precipitated tartrate. The result showed, as is natural, that the action is not altered by the presence of sulphates, which must be present when Fehling's solution is prepared in the ordinary way, for the ratio of total NaOH to CuSO, was 3.17:1, or that of the extra NaOH to CuC₄H₄O₆ was 1.17:1. The fact that there was a considerably larger relative volume of water present in this case may explain the small difference between it and the other experiments, for cupric tartrate has a distinct, although small, solubility of its own. which is given as 1 in 1700 in Watts' Dictionary. If an approximate correction for this is applied, it is evident from all the experiments that the true ratio for the action producing the neutral blue salt is very close to NaOH: $CuC_4H_4O_6 = 1.25:1$.

This result was confirmed by preparations on a larger scale in which both caustic soda and caustic potash were used for the solution of pure cupric tartrate. Thus it was found necessary to employ 325.5 c.c. of normal caustic soda for the complete solution of 54.18 grams of the salt, and 331.0 c.c. of normal caustic potash for that of 56.02 grams, giving the ratios respectively as 1.27 and 1.25 (as compared with Kahlenberg's potash ratio, namely, 1.26), the action with litmus showing that there was a slight excess of alkali used in the former case.

These synthetical experiments, read in the light of the second

lectrolytic experiment, which suggested that a tartrate is formed at the same time as a blue cuprotartrate, make it probable that the action may be such as is expressed by the equation:

$$5 \operatorname{NaOH} + 4 \operatorname{CuC_4H_4O_6} = \operatorname{Na_2C_4H_4O_6} + \operatorname{Na_3C_{12}H_7Cu_4O_{18}} + 5 \operatorname{H_2O},$$

in which, however, the formula of the second product may require modification by the inclusion of more or less of the $5\mathrm{H}_2\mathrm{O}$. That such an equation really expresses the reaction has been fairly well established by the analytical work to be described in the sequel.

Potassium and Sodium Cuprotartrates.

When about twice the volume of strong alcohol is added to the deep blue neutral solution obtained as already described, a crystalline blue precipitate separates, leaving a colourless, supernatant liquid. the solution prepared with caustic potash, instead of caustic soda, is used, the blue salt tends to separate as a gummy mass, but this may be avoided by adding the alcohol gradually. It was found, in both cases, that the clear liquid, on standing, yields a growth of delicate, colourless acicular crystals. A complete separation of these from the blue salt is easily accomplished by washing the latter repeatedly with dilute alcohol (2 vols. alcohol to 1 vol. water) in which it is quite insoluble, so that there is no difficulty in obtaining the cuprotartrate in a pure state. The colourless crystals obtained in the caustic soda reaction were carefully tested by comparison with sodium tartrate crystallised from dilute alcohol and also by conversion into the calcium and silver salts, and their identity with sodium tartrate was thus placed beyond question. The quantity of this product is always small in comparison with that of the blue salt, and, so far as could be judged without exact quantitative estimation, the proportion is in keeping with requirements of the equation just given.

The purified cuprotartrates of the alkali metals are freely soluble in water, giving perfectly neutral solutions of the characteristic deep blue colour. Although precipitated by alcohol, they contain water of crystallisation, which they lose, or partly lose, at 100°; anhydrous salts cannot be prepared in this way, however, as the dehydration is accompanied by a decomposition involving formation of cuprous oxide, which subsequently separates on treatment with water. This reducing action also occurs to an appreciable extent when the fresh solution of the pure salt is boiled for a few minutes, or when it is left at the ordinary temperature for a few days. The solid sodium and potassium salts apparently differ in their degree of hydration; the former may be exposed to the atmosphere without change, but the

latter slowly deliquesces and forms dark blue, oily drops which eventually form an enamel-like solid. When a solution of the potassium salt is poured over a smooth plate, it rapidly dries to a glassy, blue varnish which cracks off in a form exactly similar to that of the so-called scale preparations of the British Pharmacopæia, and differing from them only in colour. This behaviour is doubtless due to the formation of a higher hydrate than the crystalline one obtained by precipitation with alcohol.

When heated below redness, these salts undergo rapid decomposition, and scatter in a manner suggestive of mercury sulphocyanate, leaving a residue of mixed alkali carbonate and copper oxide.

The potassium salt, precipitated and purified by alcohol, dried on a porous tile, and subsequently left for eight days over sulphuric acid in a vacuum, was analysed in the following manner. Two portions were used for combustion which gave the total hydrogen and all the carbon not retained as carbonate in the residue. This residue could not be weighed, as it was impossible to prevent it from scattering beyond the Two other portions were very carefully heated in porcelain boat. covered porcelain crucibles and finally ignited strongly without the The residues, after weighing, were dissolved in nitric acid, and the solutions used for estimating the copper by electro-deposition and the potassium as sulphate. In all four experiments, it was found that the porcelain boat or crucible was slightly attacked. This meant necessarily a higher percentage of carbon in the combustion than that calculated from the formula and a correspondingly smaller amount of carbon in the residue, since some of the carbonate of the latter was converted into silicate. The difficulty could hardly be avoided, as it was thought unsafe to use platinum: it seemed fairest, therefore, to calculate the CO of the residue, not from the equivalent of the K₀O, but by difference after deducting the K₀O and CuO; its quantity was insufficient for direct estimation.

- I. 0.3496 gave 0.1864 CO₂ and 0.0644 H₂O.
- II. 0.4639 , 0.2448 CO₂ , 0.0860 H₂O.
- III. 0.9895, on ignition, gave 0.5569 residue, yielding 0.2804 Cu and 0.2944 K₂SO₄.
- IV. 0.7855, on ignition, gave 0.4344 residue, yielding 0.2216 Cu and 0.2338 K_2SO_4 .

These figures give the percentage results tabulated below. Consideration of the carbon results and of the figures for the residues after ignition show that the action of the alkali carbonate on the porcelain fully explains the only notable discrepancies between the found and calculated values.

	I.	11.	III.	IV.	Means.	Calcu- lated.
K			13.33	13.34	13.33	13.03
Cu			28.34	28.39	28.36	$28 \cdot 24$
C'	14.54	14.39		_	14.47	13.98 }
C"			1:30	1.16	1.23 ∫	2.00 }
H	2.05	2.06		_	2.05	1.90
0				_	(40.56)	40.85
					100.00	100.00
Residue after } ignition	_	_	56·3 8	55.32	55.85	58.33

The calculated percentages are those corresponding to the formula, $K_sC_{12}Cu_4H_7O_{18}+5H_2O$, already suggested by the synthetical experiments; it may, therefore, be regarded as established, although the possibility exists that a portion of the $5H_2O$ is present, not as water of crystallisation, but as part of the acid radicle.

Insoluble Cuprotartrates.

A solution of potassium or sodium cuprotartrate gives insoluble, or sparingly soluble, amorphous precipitates when mixed with solutions of the following salts:—

Ba(NO₃)₂. Granular, light blue precipitate, soluble in excess of the alkali salt.

 ${\bf AgNO_3}$. Light blue precipitate, very sparingly soluble in water; decomposes on exposure to light.

Pb(NO₈)₂. Light blue precipitate, very sparingly soluble in water, or in excess of either solution.

CuSO₄. Blue precipitate, darker than any of the others; fairly soluble in water and in excess of the alkali salt; not formed with dilute solutions.

ZnSO₄. Light blue precipitate; more soluble than the copper salt.

FeCl₈. On slowly adding dilute ferric chloride solution, the following characteristic changes occur: first a green solution is formed, then a bright green precipitate, dissolving in excess to a clear yellow solution, which, on standing, quickly deposits a copious yellow precipitate.

Whilst the last of these reactions probably involves more complicated changes, the others seem to depend simply on the formation of cuprotartrates, in which the heavy metals take the place of the potassium or sodium of the blue soluble salt. Only the lead and silver salts have been examined with much care as yet, and of the others

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the copper cuprotartrate is interesting as presumably containing the same metal in two capacities.

Lead Cuprotartrate was prepared by precipitating the potassium salt with lead nitrate solution. The precipitate, after thorough washing, was dried over sulphuric acid in a vacuum, and when analysed gave numbers which indicated that its composition corresponded to that required for the formula $Pb_8(C_{12}H_9Cu_4O_{10})_2 + 24H_2O$. It is doubtful, however, whether the salt examined can be regarded as a definite hydrate, and, moreover, it contained some impurity, probably lead nitrate, arising from the well known habit that some precipitates have of carrying down soluble salts and refusing to part with them on washing.

Silver Cuprotartrate.

This was prepared by adding silver nitrate solution to potassium cuprotartrate, a rather large excess of the former being found necessary for complete precipitation. It was washed, dried on a porous tile, and placed in a vacuum desiccator for two days, the work being carried out in a dark room, as it was found necessary to guard the salt from the action of light. Two portions were then subjected to combustion, and the residue from one of these was dissolved in nitric acid for the estimation of silver as chloride and of copper electrolytically after removal of chlorine. A third portion was ignited and used similarly for silver and copper estimations, another portion being employed for estimating the water lost by heating at 100° in the dark for 2 hours, no further loss occurring after heating for an additional $2\frac{1}{2}$ hours.

- I. 0.6530 salt gave 0.2840 CO, and 0.1331 H,O.
- II. 0.7869 , , 0.3451 CO₂ 0.1605 H₂O, and 0.4194 residue, which gave 0.2704 AgCl and 0.1724 Cu.
- III. 0.7663 salt, on ignition, gave 0.4102 residue, which gave 0.2643 AgCl and 0.1663 Cu.
- IV. 0.5997 lost 0.0807 H₂O.

	I.	II.	I II .	IV.	Means.	Calculated.
Ag		25.86	25.90	_	25.89	27.04
Cu	_	21.91	21.70		21.80	21.25
C	11.87	11.96			11.92	12.02
H	2.27	2.26	-		2.26	$2 \cdot 27$
0				_	(38·13)	37.42
					100.00	100.00
Residue on ignition		53.30	53.53		53.42	53.65
Water lost	} —	-		13.45	13.45	13.54

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The calculated percentages are those required for the formula ${\rm Ag_3C_{12}Cu_4H_9O_{19}+9H_2O}$, or for the formula ${\rm Ag_3C_{12}Cu_4H_7O_{18}+10H_2O}$ on the assumption that the salt retains one molecular proportion of water of hydration after drying at 100° . At any higher temperature, the salt is decomposed and darkened in colour. It is evident, from the proportions of silver and copper found, that the preparation was not quite pure, but the figures, on the whole, seem to confirm the formula, and may be taken as indicating that the radicle of the cuprotartrates is either $({\rm C_{12}Cu_4H_7O_{18}})'''$ or $({\rm C_{12}Cu_4H_9O_{19}})'''$, so that of the water indicated in the formula for the potassium salt at least $4{\rm H_2O}$ are present as water of crystallisation.

The conclusion may thus be drawn, that the cuprotartrates are metallic salts of a definite trivalent radicle $(C_{12}H_7Cu_4O_{18})^{\prime\prime\prime}$ or $(C_{12}H_9Cu_4O_{19})^{\prime\prime\prime}$, and since none of the salts has been obtained with less hydrogen and oxygen than that indicated by the second formula without at the same time undergoing general decomposition, this may be accepted for the present, at any rate, as correct. In this case, the formulæ of the potassium salt, dried in a vacuum, and of the silver and lead salts dried at 100° , are respectively, $K_8C_{12}H_9Cu_4O_{19}, 4H_2O$, $Ag_3C_{12}H_9Cu_4O_{19}$, and $Pb_8(C_{12}H_9Cu_4O_{19})_2$.

Instability of Cuprotartaric Acid.

Some attempts have been made to isolate cuprotartaric acid itself, but so far without success. When a solution of the potassium salt is titrated with a dilute mineral acid, the deep blue colour gradually gives place to the colour of an ordinary copper salt solution, and when this change is complete, or nearly so, a light blue precipitate slowly forms which has the appearance and characters of cupric tartrate. One sample, prepared in this way, was analysed and proved to be slightly impure cupric tartrate. Its formation may be represented by the equation:

$$\mathbf{K_{3}C_{12}H_{9}Cu_{4}O_{19}} + 5\mathbf{HCl} = 3\mathbf{KCl} + 3\mathbf{CuC_{4}H_{4}O_{6}} + \mathbf{CuCl_{2}} + \mathbf{H_{2}O}.$$

As the precipitate is produced slowly, it is possible that this decomposition is really preceded by the formation of a very unstable cuprotartaric acid, $H_3C_{12}H_9Cu_4O_{19}$, which then reacts with more acid:

It seemed possible that a solution of the free acid might be obtained without decomposition by suspending the lead salt in water and adding just sufficient dilute sulphuric acid to remove the lead as sulphate, but this also proved unsuccessful. The pale blue solution was proved to contain positive cupric ions, and no complex blue

negative ions, by electrolytic experiments similar to those described at the beginning of this paper.

Sulphuretted hydrogen solution decomposes all the cuprotartrates, precipitating cupric sulphide or a mixture of this with the sulphide of the other metal. The ease with which this occurs is a little surprising, as truly negative metallic radicles do not generally break up in this way. Indeed, in this reaction, the copper of the cuprotartrates shows in marked contrast to, say, the gold of the aurocyanides, yet the electro-negative character of the one is as certain as is that of the other. But it seems to be only the ion that can exist as such, whilst the un-ionised hydrogen cuprotartrate tends to undergo such transformation as to turn the copper back into an ordinary metallic radicle. If this is so, the action of sulphuretted hydrogen, even on the potassium salt, is explained, since a proportion of the hydrogen and cuprotartaric ions must naturally enter into combination, and more must unite to take the place of this when it is transformed.

Kahlenberg (loc. cit.) adduced arguments, based on physical properties, in favour of the view that the excess of alkali in Fehling's solution as usually made, or part of it, is present in the state of combination, and not merely mixed with the blue salt. We have obtained chemical evidence in proof of the truth of this contention, as the addition of alcohol to a solution made from caustic soda and cupric tartrate in the ratio $2\text{NaOH}: \text{CuC}_4\text{H}_4\text{O}_6$ throws out a strongly alkaline salt which retains this character even after the alcoholic washings have become quite neutral, and contains sodium and copper in the ratio Na: Cu = 7:4. We intend to continue this investigation, and in the meantime abstain from any discussion of the probable or possible inner constitution of the negative radicle of the cuprotartrates.

THE UNIVERSITY OF MELBOURNE.

LXX.—The Allotropic Modifications of Phosphorus.

By DAVID LEONARD CHAPMAN, B.A.

It is generally believed that there are at least three distinct allotropic modifications of phosphorus, namely, the transparent, red, and metallic varieties. The transparent variety may be converted into the red most conveniently by the action of heat; this change takes place with tolerable rapidity, at a temperature of from 240° to 250°, but still more readily at a higher temperature or if traces of certain impurities, such as iodine, are present. The same change may be effected by the

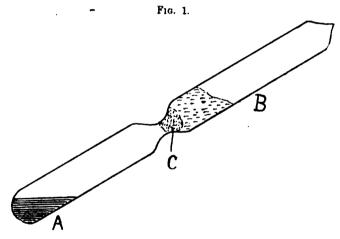
action of sunlight at ordinary temperatures. Pedler (Trans., 1890, 57, 599) has shown that amorphous phosphorus is formed by the action of tropical sunlight, even on a solution of ordinary phosphorus in carbon bisulphide, and that when obtained in this way it is all vellow powder changing gradually to red. Amorphous phosphorus is also sometimes formed at the ordinary temperature in certain chemical reactions: it may be obtained, for instance, by the action of oxalic acid on phosphorus trichloride as a yellow powder, which, on exposure to the air for some time, becomes red. Metallic phosphorus, the supposed third variety, was first obtained by Hittorf (Pogg. Ann., 1865, 126, 193), who heated lead and phosphorus in a sealed tube at a temperature approaching a red heat for 10 hours, and afterwards removed the lead with nitric acid of specific gravity 1:1. Pedler believes that this third variety is only red phosphorus, but he has left unanswered certain very strong evidence derived from the vapour tension and supporting the view that there are three varieties. Brereton Baker (Phil. Trans., 1888, 179, 571) has shown that vapour is emitted from red phosphorus at a temperature approaching that of boiling mercury, and that below this temperature the phosphorus is unaltered; this was done by introducing one end of an exhausted tube containing red phosphorus into the vapour of boiling mercury, a small quantity of ordinary phosphorus condensing at the cool end of Pedler has noticed the same fact. The temperature at which metallic phosphorus begins to be converted into vapour is also that of boiling mercury, so that in this particular the two varieties resemble one another.

Evidence adduced from Appearance.—Pedler has examined commercial red phosphorus, the yellow variety obtained by the action of light on a solution in carbon bisulphide, and metallic phosphorus under the microscope, and from the facts that they all consist of transparent particles of varying size, that the colour which they present to the naked eye depends on the size of the particles, and that the action of all the varieties on polarised light is the same, he concludes that red and metallic phosphorus are identical, a conclusion which is supported by the following experiments.

Preparation of Metallic Phosphorus.—This substance is formed by dissolving phosphorus in lead at a high temperature, and, according to Hittorf (loc. cit.), separates in microscopic rhombohedra in the lead on cooling. Pedler states that it may be formed more easily by projecting amorphous phosphorus into lead at a somewhat high temperature. Both methods are open to the objection that the amorphous phosphorus may only have mixed with the lead, and this may account for the similarity of properties observed by Pedler in red and metallic phosphorus. In order to obviate the objection, an experi-

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ment was arranged in such a manner that the lead only came into contact with the vapour of phosphorus. If a substance and its vapour are soluble in a common solvent, both are equally soluble, so that if metallic phosphorus is formed by Hittorf's method, it must also be formed when the vapour alone comes into contact with the lead. A hard glass tube was drawn out as in the diagram. The compartment A contained pure lead, and a plug of glass wool was rammed tightly down against the constriction C. Amorphous phosphorus was introduced into the compartment B, and the tube, after being exhausted and sealed, was placed in an iron tube and heated to dull redness in an inclined position. After cooling, the lead was removed by nitric acid of specific gravity $1 \cdot 1$, and a black powder remained behind; this, when examined on a slide under the microscope, was found to consist of black, opaque masses, which, if lightly pressed against the slide,



separate into exceedingly minute, regular, transparent particles, all of approximately the same size, and so small that it is impossible to assert with confidence what their exact shape is; they have, however, two pairs of parallel edges, and are probably cubes or rhombohedra.

Hittorf states that metallic phosphorus may also be formed by heating amorphous phosphorus at the temperature of boiling phosphorus pentasulphide and condensing the vapour at the temperature of boiling sulphur. I performed a similar experiment. An exhausted tube containing red phosphorus was placed in the vapour of boiling phosphorus pentasulphide. With any liquid of high boiling point, the vapour at the bottom of the vessel is always at a higher temperature than that at the top, unless special precautions are taken, and so in my experiment, after several hours heating, amorphous phosphorus

was deposited at the top of the tube in a yellowish-red layer. The tube was opened under carbon bisulphide to dissolve the ordinary phosphorus, and the layer of red phosphorus on the glass, when examined under the microscope, was found to consist of crystals of the same size and shape as those formed by crystallisation from lead.

Red phosphorus obtained by the action of sunlight, after purification from ordinary phosphorus by carbon bisulphide, and the yellow variety obtained by the action of phosphorus trichloride on oxalic acid, were also examined under the microscope, and were found to consist of similar microscopic particles. The yellow colour of the variety obtained from phosphorus trichloride and oxalic acid is due to the more complete separation of the crystals; these, after exposure to moist air, stick together, and the yellow colour changes to red. In the cases which I have examined, the darker colour of some specimens of red phosphorus was always due to the aggregation of the microscopic rhombohedra, and not to the varying sizes of the crystals.

Commercial red phosphorus consists of irregular masses of varying sizes. When treated with caustic soda or carbon bisulphide, or heated in a vacuum, no alteration in appearance is noticeable. If, however, it is boiled with caustic soda and then with hydrochloric acid, a fine powder rises to the surface of the acid, and, when examined under the microscope, presents the same appearance as the variety known as metallic phosphorus.

The crystalline form of metallic and of red phosphorus is therefore the same. The crystals of red phosphorus, however obtained, are very uniform in size; commercial red phosphorus consists of these microscopic crystals so firmly cemented together by the action of moist air that they form brittle blocks with a metallic lustre, the crystals being probably held together by an oxide or acid of phosphorus. Ordinary phosphorus is not present, as vapour is not given off in a vacuum until a temperature of 358° is reached.

Evidence for the Existence of Two Distinct Varieties of Red Phosphorus.

Hittorf (loc. cit.) has shown that, when amorphous phosphorus is heated for 8 hours in a sealed tube at the temperature of boiling sulphur, the vapour tension at first rises and then falls, and that during the operation the specific gravity of the phosphorus increases. This he explains by assuming that there are two distinct forms of red phosphorus, and that the change from one variety to the other takes place gradually at the temperature of boiling sulphur.

Lemoine (Compt. rend., 1871, 73, 797) examined this point also, and found that when white phosphorus is heated in a closed glass bulb in the vapour of boiling sulphur it is first converted into red, and then

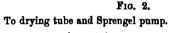
the vapour tension falls very gradually until it arrives at the limit of 3.6 grams of vapour per litre. When red phosphorus is heated in a closed vessel under similar circumstances, the vapour tension gradually rises, the rate of increase depending on the amount of amorphous phosphorus present at the beginning; if the amount originally present is more than 16 grams per litre, the vapour tension at first rises and then falls, whilst with 30 grams per litre it rises as high as 4.7 grams, and finally falls to the limit, or 3.7 grams per litre. Lemoine attributes the temporary rise in tension to an alteration of the surface similar to the polarisation of electrodes. The facts, however, admit of an explanation identical with that given by Hittorf-namely, that the phosphorus is very gradually converted into another form, the vapour tension of which is lower. Under these circumstances, the excess of vapour formed by the evaporation of the less stable form would be gradually condensed to the new variety, after the change in the solid had taken place.

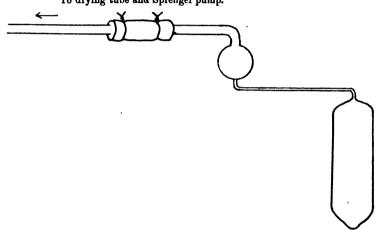
The facts therefore at first sight appear to support the view that there are two distinct forms of red phosphorus.

Experiments devised to clear up this point lead to the conclusion that the temporary rise of vapour tension is not due to a change of state, but to the presence of compounds of phosphorus, which decompose at the temperature of boiling sulphur giving, amongst other products, phosphorus vapour. In all the experiments, bulbs of about 30 c.c. capacity were employed, and about 1 gram of red phosphorus was introduced into them. The bulb communicated by a capillary tube with a drying tube containing phosphorus pentoxide, and then with the Sprengel pump; the phosphorus and bulb may thus be dried in a vacuum at any required temperature. When dry, the bulb is closed, and suspended by means of a platinum wire in sulphur vapour, the bath consisting of a porcelain tube, similar to the water tube of Victor Meyer's vapour density apparatus, the part above the bulb being jacketed with asbestos as recommended by Callendar (Phil. Trans., 1891, 182, 119). After removal of the bulb from the bath, the vapour of phosphorus condenses in perfectly colourless drops quite free from the red modification. The bulb, when cold, is opened under carbon bisulphide, the solution filtered from amorphous phosphorus, and the carbon bisulphide distilled off in the presence of aqua regia. A small quantity of trichloromethylsulphonic chloride is formed during this operation. No phosphorus could be detected in the distillate of carbon bisulphide, although, by several blank experiments, it was shown that phosphorus, when dissolved in carbon bisulphide, may be very accurately estimated by evaporating almost to dryness with aqua regia, and precipitating the phosphoric acid, first with ammonium molybdate, and then twice with magnesia mixture, with the ordinary

precautions. When the bulb is first exhausted, a gas smelling like phosphoretted hydrogen, is evolved, and can only be completely expelled by heating for half an hour at the temperature of sulphur vapour in a vacuum. Commercial red phosphorus therefore is not pure, but contains some compound which, by the action of heat and reduced pressure, decomposes with the formation of phosphoretted hydrogen. It is probably this compound which binds the microscopic crystals so firmly together.

Three series of experiments on the vapour tension were performed. In the first, commercial red phosphorus, which had been exposed to the air, was used. In the second, phosphorus which had been purified





by boiling with caustic soda was employed, the caustic soda being removed by washing successively with hydrochloric acid and water, the phosphorus was then rapidly dried on a porous plate and afterwards in a vacuum over sulphuric acid. In the third, the phosphorus, purified and dried in this way, was heated for half an hour in a vacuum at the temperature of boiling sulphur until gas ceased to be evolved. The results are recorded in the following table in grams of vapour per litre, the duration of the experiment being given in hours:—

i	1 hour.	2 hours.	3 hours.	4 hours.	16 hours.
Red phosphorus which had been exposed to the air	3·65 3·58	4·68 4·24 3·94	4·71 3·91	4·70 4·21	3.68

On comparing the results obtained after heating for 2 hours, it will be seen that the highest vapour tension is obtained with the impure substance; the rise in vapour tension is therefore due to the formation of phosphorus vapour by the gradual decomposition of some compound, which may be partially removed by boiling with caustic soda. When this compound has been partially decomposed by heating for half an hour in a vacuum, the vapour tension is 3.94 grams per litre, and thus approaches the limit of 3.7 grams per litre. Thorpe and Tutton have shown (Trans., 1890, 57, 545) that P_4O_6 decomposes into P_2O_4 and phosphorus at the boiling point of sulphur, and it is possible that other compounds of phosphorus may also decompose with the formation of phosphorus.

We are therefore compelled to conclude that there is only one variety of red phosphorus; firstly, from identity of appearance, and, secondly, because the higher vapour tension observed in some cases, and supposed to furnish evidence for the existence of two forms, is due to the presence of impurities.

Hittorf has shown that phosphorus vapour has the same density whether it is obtained by the evaporation of ordinary or of red phosphorus. It is important to establish this point, since no explanation of the mutual changes which occur can be given until it is settled; the density of the vapour has therefore been determined in both cases.

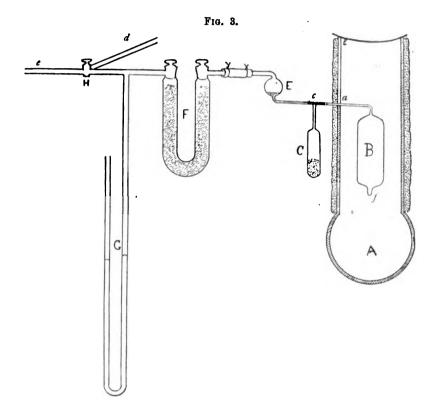
Density of the Vapour of White Phosphorus.*

The molecular weight found by Mitscherlich (Annalen, 1834, 12, 137) at 515° was 131.6, and by Deville and Troost (Compt. rend., 1863, 56, 891) at 1040° was 129.3. From these results, it was thought probable that a further condensation of the molecule might take place at a lower temperature. The variation from the theoretical value for P_4 at the temperatures of boiling sulphur and mercury is, however, not more than we should expect in an imperfect gas.

The vapour bath, A, consisted of a porcelain tube with a slit ab in the side through which the tube attached to the bulb B can be inserted; during the experiment, the neck of the bath is surrounded with asbestos. C contains well-dried red phosphorus; F is a drying tube containing phosphorus pentoxide. The pressure may be read off on the manometer, G; e and d lead respectively to the Sprengel pump, and to a gasholder containing nitrogen, free from carbon dioxide, and standing over sulphuric acid. The nitrogen enters d through a fine capillary tube, which enables the supply to be better regulated.

* The molecular weights calculated from the vapour density are here given in stead of the vapour density compared with air.

Before beginning an experiment, the whole apparatus is dried by first exhausting, then allowing dry nitrogen to enter and exhausting again. The phosphorus in C is then distilled into E, and when a sufficient supply has condensed, C is removed by the blowpipe. The bulb B is next heated in the sulphur vapour, the heat radiating from the burner and the bath being sufficient to keep the phosphorus in the tube melted during the experiment. The pressure



within the whole apparatus is gradually increased by allowing nitrogen to enter. The phosphorus in E is thus driven along the tube C to the entrance of the bath, where it evaporates.

When the pressure has risen sufficiently high, the tap H is closed, and the tube c, leading to the bulb, is sealed with the blow-pipe near to the entrance of the bath. The bulb B is then opened under boiled distilled water; it is always found to contain a small bubble of gas, which collects in the drawn out end of the bulb f, and may be con-

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veniently measured by making a file mark on the glass, a correction for this bubble of gas being made in the calculation. The amount of phosphorus in the bulb is determined by converting it into phosphoric acid with aqua regia, and estimating it as magnesium pyrophosphate after previous precipitation with ammonium molybdate. The advantage of this method of finding the vapour density is that no non-volatile phosphorus compounds can be introduced into the bulb, since it is the vapour only which enters, one of the chief sources of error in Dumas' determinations being the introduction of impurities.

A similar bulb of the same glass, after exhaustion, is dried by filling several times with dry nitrogen, free from carbon dioxide, while at the temperature of the bath; it is sealed when filled with nitrogen at a known pressure, the nitrogen which it contains being afterwards measured by opening under mercury. The temperature of the bath calculated from this experiment is 444.8°, 0.000008613 being taken as the coefficient of expansion of glass. From these experiments, data sufficient for calculating the density are obtained. Five determinations of the density were made, and the molecular weights calculated from them are:

127·1, 126·9, 126·7, 127·0, 126·9; mean, 126·9.

The density was also found at the boiling point of mercury, and the molecular weight calculated from it is 126.5.

Density of the Vapour of Red Phosphorus.

In these experiments, the entrance to the bulb was a very fine capillary tube, the bulb itself containing amorphous phosphorus. Since the rate at which the vapour is formed is very slow, at least one gram of red phosphorus must remain in the bulb at the end of the experiment, or a large volume of nitrogen will diffuse through the capillary. The pressure during the experiment was a little below that of the atmosphere. It is impossible to remove the bulb from the vapour-bath immediately after closing it, and during the short time it remains there the tension rises slightly, making the results too high. The amount of ordinary phosphorus remaining in the bulb was estimated, as already described, by dissolving in carbon bisulphide. The numbers obtained from five experiments were:

130.81, 131.83, 130.3, 130.7, 131.23; mean 130.97.

The density found in this way is almost 3 per cent. higher than that found with white phosphorus, but the difference is easily accounted for by the evaporation which takes place after closing. In fact, if the

experiment is conducted at a lower pressure, the molecular weight is found to be much higher, since the evaporation, during the short interval which elapses between closing and removing from the vapourbath, takes place more rapidly. The numbers, however, are sufficiently near to those obtained with ordinary phosphorus to justify the conclusion that the vapours of red and ordinary phosphorus are identical. This conclusion might also be reached by consideration of the fact that the vapour of red phosphorus condenses to ordinary phosphorus whenever the temperature is below that at which white phosphorus changes to red, and even at a temperature above it, although, in the latter case, red phosphorus is gradually deposited on the surface of the glass, whereas, if the vapours of the two varieties were different, red phosphorus would be expected whenever the evaporation was from red phosphorus.

Variation of Vapour Tension of both varieties of Phosphorus with Change of Temperature, and deductions therefrom.

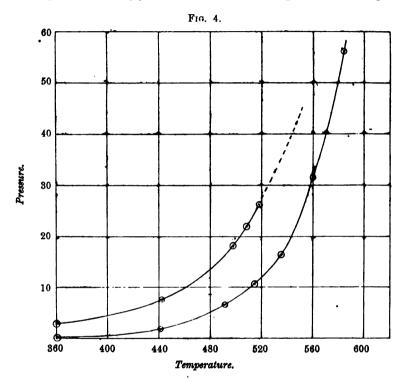
The vapour pressures supported by both varieties of phosphorus have been found by Troost and Hautefeuille (Compt. rend., 1873, 76, 219) for a considerable range of temperature, and are shown in curves (Fig. 4). It will be noticed that the two curves approach one another, so that at a higher temperature it may be expected that they will meet. At the temperature and pressure of the point of intersection, both varieties ought to exist together—that is, the red ought to melt, forming the ordinary modification. This anticipation has been realised experimentally by heating red phosphorus in sealed capillary tubes of hard glass, as, at a temperature near to the fusing point of potassium iodide, red phosphorus melts to a colourless liquid exactly similar in appearance to ordinary phosphorus, although the temperature is far above that at which the colourless variety changes readily to the red.*

Not a single instance has yet been recorded of red phosphorus changing directly into white below its melting point, although the converse change may be effected by the action of light, heat, or pressure; indeed, the only way to change red phosphorus into white is, indirectly, through its vapour. The facts therefore lead to the conclusion that at the ordinary temperature, and below the melting point, red phosphorus is stable, whilst the white modification is unstable, being liable to change into it.

The correctness of this conclusion may be demonstrated. Let a_1T

^{*}Hittorf (loc. cit.) states that amorphous phosphorus cannot be melted when heated to redness in a sealed tube. An ordinary sealed tube will not stand the pressure.

(Fig. 5) be the equilibrium curve for ordinary phosphorus and phosphorus vapour on the pressure temperature diagram, and a_2T the corresponding curve for red phosphorus and vapour. Since all three states exist at T, the white phosphorus | red phosphorus curve must pass through this point. Experimental determination of the latter curve would no doubt prove exceedingly difficult, but its relative position with respect



to the curves a_1T and a_2T may easily be found. Let v_1 , v_2 , v_3 be the volumes of unit mass of red phosphorus, white phosphorus, and the common vapour respectively. Then v_1 , v_2 , and v_3 are in ascending order of magnitude. Let $\left(\frac{dp}{dT}\right)_1$, $\left(\frac{dp}{dT}\right)_2$, and $\left(\frac{dp}{dT}\right)_3$ be the slopes of the curves a_1T , a_2T , and a_3T respectively, at the triple point T. Then at the triple point,

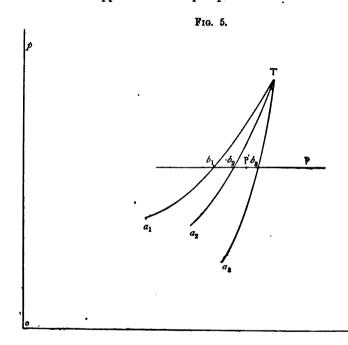
$$(\boldsymbol{v}_1-\boldsymbol{v}_2)\!\!\left[\!\left(\frac{dp}{dT}\!\right)_3\,-\,\left(\frac{dp}{dT}\!\right)_2\right]\!=\!(\boldsymbol{v}_3-\boldsymbol{v}_2)\!\!\left[\!\left(\frac{dp}{dT}\!\right)_1-\!\left(\frac{dp}{dT}\!\right)_2\right]\!\!.^{\Phi}$$

Since v_1 , v_2 , and v_3 are in ascending order of magnitude, $v_1 - v_2$.

* Le Potentiel Thermodynamique et ses application.—M. Duhem.

and $v_8 - v_2$ must have opposite signs, consequently $\left(\frac{dp}{dT}\right)_3 \quad \left(\frac{dp}{dT}\right)_2$ and $\left(\frac{dp}{dT}\right)_1 - \left(\frac{dp}{dT}\right)_2$ must have opposite signs, and therefore $\left(\frac{dp}{dT}\right)_2$ must lie between $\left(\frac{dp}{dT}\right)_1$ and $\left(\frac{dp}{dT}\right)_3$, consequently the curve must be situated as in the figure, with Ta_2 between Ta_1 and Ta_3 .

Draw the horizontal line b_1 , b_2 , b_3 cutting the curve Ta_1 , Ta_2 , Ta_3 , and let it be supposed that red phosphorus is in such a condition that



it is represented by the point P. Since this point is not on the curve a_3T , the phosphorus is in a condition of unstable equilibrium. Moreover, the point P is to the right of the curve a_3T , and therefore any change which takes place must be one accompanied by an absorption of heat*; in other words, it must be a change from red to white phosphorus; but the point P is also to the right of Ta_1 and Ta_2 , and therefore both the red phosphorus and white phosphorus formed from it must be simultaneously changed into vapour. Since the white phosphorus is a liquid, it will be converted into vapour immediately it is formed. As the curve a_3T is almost vertical, P cannot be much below the temperature at the triple point, and therefore red phos-

^{*} Le Potentiel Thermodynamique et ses application.-M. Duhem.

phorus can be converted into white only at a temperature (the fusing point of potassium iodide) near to the triple point; and even at this temperature, if the pressure is below that at the triple point, the white phosphorus will evaporate so rapidly that it will be impossible to prove its presence except by showing that there is a sudden increase in the rate of evaporation immediately we pass across the curve a_8T .

An attempt was made to find the point b_3 experimentally, when the line $b_1b_2b_3$ represents atmospheric pressure (that is, the melting point of amorphous phosphorus at atmospheric pressure) by observing the rate at which phosphorus distils; but although the vapour was formed quite slowly as the temperature was rising, the rate of increase in evaporation at this point was so rapid that explosion invariably occurred in the tube, a result to be expected in the case of a solid melting far above the boiling point of the liquid.

For any point P' to the left of a_3T the change is from white to red phosphorus, and, since Ta_3 is almost vertical, we may say that for any temperature not far below the melting point of potassium iodide white can change to red phosphorus, but not vice versa. It is therefore incorrect to assert that red phosphorus is changed into white phosphorus at the boiling point of mercury; to be correct, we should say that red phosphorus is converted into vapour at that temperature.

It has been asserted above that red phosphorus can be converted into white phosphorus only at a temperature approaching the melting point of potassium iodide; this does not mean that red phosphorus cannot be converted into vapour below this temperature and then condensed to the liquid, but that the direct change is impossible.

On referring to the curves (Fig. 5) it will be seen that they are identical with the equilibrium curves for a solid and vapour, liquid and vapour, and solid and liquid below the triple point, and as a liquid is in the superfused condition below the triple point, we must regard melted ordinary phosphorus as superfused red phosphorus. Red phosphorus therefore exhibits the phenomenon of superfusion to a much more remarkable degree than the ordinary variety.

Conclusions.

(1) Metallic phosphorus and red phosphorus are identical. This is proved by their similarity in appearance when viewed under the microscope. The higher vapour tension attributed to some varieties of red phosphorus is due to impurity, which on heating decomposes, forming phosphorus vapour.

(2) The vapours of red and ordinary phosphorus are identical. The vapour density of ordinary phosphorus at the temperature of boiling

sulphur and mercury has been found to agree closely with the density calculated on the assumption that the molecule consists of four atoms, although the results obtained by Mitscherlich and by Deville and Troost at higher temperatures would scarcely seem to make this probable.

(3) Red phosphorus melts, changing into ordinary phosphorus, under pressure, at the melting point of potassium iodide. This point on the pressure temperature diagram, I propose to call the triple point of red phosphorus. Melted ordinary phosphorus thus becomes superfused red phosphorus, and superfused ordinary phosphorus becomes the superfused liquid of both varieties. As at ordinary temperatures the red modification is stable and the white unstable, phosphorus appears to have in a remarkable degree the property of remaining in an unstable condition.

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LXXI.—Oxidation of Furfuraldehyde by Hydrogen Peroxide.

By C. F. Cross, E. J. BEVAN, and THV. HEIBERG.

THE investigations dealt with in this communication are part of a scheme of research undertaken to extend our knowledge of the interactions of hydrogen peroxide and typical carbon compounds, in view of their remarkable character, not only from the nature of the products, but also from their dependence upon the presence of inorganic oxides or salts of a certain type. We need only mention the researches of H. J. H. Fenton on the oxidation of tartaric acid (Trans., 1894, 65, 899; 1895, 67, 48; 1896, 69, 546), and the later developments, which, since we associated ourselves with him, have led to a more extended survey of the possibilities suggested by his work; these comprise the oxidation of typical carbohydrates (Cross, Bevan and Smith, Trans., 1898, 73, 463; Morrell and Crofts, Proc., 1899, 15, 99), the oxidation of polyhydric alcohols of the general formula CH₂(OH)·(CH·OH)_n·CH₂·OH by Fenton and Jackson (Trans., 1899, 75, 1), and the oxidation of calcium gluconate to d-arabinose by O. Ruff (Ber., 1899, 32, 550), the last-named being the first successful attempt to pass by well defined processes of oxidation from a hexose to a pentose. The very large yield of the pentose obtained by Ruff is noteworthy as showing that the actions of hydrogen peroxide are capable of very definite regulation and control; it may be pointed out, however, that he omitted to determine the total yield of pentose by distilling with hydrochloric acid and estimating the furfuraldehyde obtained. From these typical cases, the transition to furfuraldehyde is obvious in view of its connection with a very widely distributed and complex group of plant constituents; and our investigations contribute another item in elucidating the chemistry of the lignocelluloses.

In the extensive literature bearing on the problem of the constitution of hydrogen peroxide, of which a fairly complete survey may be obtained from the obituary notice of M. Traube (Ber., 1896, 29, 1106), reference to its actions on carbon compounds are conspicuously absent, for the reason that these have been limited for the most part to those which we may term microchemical curiosities. The conclusion has been reached mainly from the study of the conditions under which hydrogen peroxide is produced, and its reactions with inorganic compounds, that the formula H_cO_cO is distinctly at variance with its constitution, and that it is to be regarded rather as a product of direct union of hydrogen and oxygen, the above formula being permissible only when written as a thermal expression, (H_oO_iO) = -23.07 Cal. Whilst the endothermic nature of the compound conveys many suggestions of special modes of action, it is in its reactions with carbon compounds that we may expect to ascertain whether the constitution of the peroxide is to be represented to one or other of the forms (HO·OH), (H₀,O₀), or (H₀O₁O). Now, in the case of furfuraldehyde we find that, together with oxidation products, methylated derivatives are formed in relatively large quantity, their formation in small quantity in the interactions of the carbohydrates and the peroxide having already been established. This effect can only be explained as the result either of a migration of an electrolytic character within the molecule of the carbon compound under the influence of the peroxide, or of a tendency of the peroxide to break up into H₂ and O₂. The latter hypothesis seems to be more consistent with the facts, and also explains why the typical CO-group in the aldehydic compounds under investigation is much less readily attacked than the hydrogen of the CH-group in immediate contact with it. The results of the present investigation comprise the production of a monohydroxyfurfuraldehyde with a relatively small quantity of the corresponding carboxylic acid, and lend no support to the 'hydroxyl' view of the constitution of the peroxide.

As this paper is intended as a preliminary communication on a subject which necessarily opens up a number of issues, and is beset with no little difficulty, we do not propose to discuss minutely the constitutional and other problems involved. The experimental results are sufficiently definite to warrant publication, and the conclusions to which they lead are so far well grounded as to clearly define the nature

of the problem, which we hope to solve finally by the further investigations which are being actively prosecuted.

EXPERIMENTAL.

Hydrogen peroxide is added in successive quantities to furfural dehyde in 2—3 per cent. aqueous solution containing a small quantity of ferrous sulphate, until the characteristic reaction of the aldehyde with an iline acetate can be no longer obtained. At the ordinary temperature, the oxidation is extremely slow, but it is rapid at 40°, and the proportion of the peroxide taken up is from 2 to 3 mols. $\rm H_2O_2$ to each mol. of the aldehyde. The solution becomes distinctly acid, and gives the following characteristic reactions:

- (1) With phenylhydrazine acetate in the cold, a copious bright reddish-orange precipitate.
- (2) With phloroglucinol and hydrochloric acid, a deep magenta to purple solution, closely resembling that obtained with the lignocelluloses; this, when heated, gives a copious precipitate of the condensation product, which dissolves in alcohol, forming an intense violet solution.
- (3) With resorcinol and hydrochloric acid, a violet colour changing to a greenish-blue on warming, and exhibiting in this respect the closest similarity to the lignocelluloses.

The Hydrazine Derivative.—This proved on investigation to be a hydrazone, and the yield from two independent experiments, each representing 1 gram of furfuraldehyde, amounted to 1.8 and 1.9 grams of hydrazone respectively, indicating that the compound is the main product of the reaction. The hydrazone obtained by direct precipitation could not be separated satisfactorily unless the acid products in the solution had been removed previously by precipitation as barium salts. When dry, it was treated exhaustively with hot benzene, and the residue, after drying, was dissolved in alcohol, and the hydrazone separated by adding water to the filtrate.

0.2794 gave 0.6692 CO₂ and 0.1227 H₂O. C=65.33; H=4.92. 0.3000 ,, 34.8 c.c. of nitrogen at 18° and 742.9 mm. N=13.10. $C_5H_4O_2$:N₂HPh requires C=65.35; H=4.95; N=13.80 per cent.

It is evident, from the characteristic reactions of the original aldehyde, that it is a furfuran derivative, and the above formula represents the hydrazone of a monohydroxyfurfuraldehyde, C₄OH₂(OH)·COH.

The Acid Products of Reaction.—Of these, the most characteristic is an acid which is easily isolated, as it forms barium and lead salts insoluble in acetic acid. The salts are obtained as crystalline precipitates, and contained barium and lead in the relative proportion Ba: Pb. The barium salt was prepared both in presence of acetic

acid and by precipitation from solutions previously neutralised, and it was found that the composition of the salt was not affected by this variation of the conditions under which it was formed.

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0.1896 gave 0.1146 BaSO<sub>4</sub>. Ba = 35.55.
0.4552 ,, 0.5145 CO<sub>2</sub> and 0.0893 H<sub>2</sub>O<sub>5</sub>. C = 30.83; H = 2.19.
(C<sub>5</sub>H<sub>3</sub>O<sub>4</sub>)<sub>2</sub>Ba requires C = 30.69; H = 1.53; Ba = 35.04 per cent.
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The numbers agree with those required for a hydroxypyromucic acid, C₄OH₂(OH) COOH, and confirm the conclusions drawn from the examination of the hydrazone that the main reaction of the peroxide with furfuraldehyde leads to the substitution of the OH-radicle for a hydrogen atom.

The acid products were studied more completely by fractionally treating the solution with lead acetate (1) in presence of acetic acid; (2) in neutralised solution [filtrate from (1)]; (3) with the basic acetate [filtrate from (2)]. It seemed possible that, under the last condition, the hydroxyfurfuraldehyde itself would be precipitated, but this was not the case. From the fraction (2), on decomposing the lead salt, we obtained small quantities of acids having the characteristic properties of hydroxyketonic acids, but beyond the acid just described, none is formed in such quantity or with such properties as admit of its ready isolation. The hydroxypyromucic acid, moreover, is formed only in relatively small quantity, as the yield of its barium salt is only about 5 per cent. of that theoretically possible from the amount of furfuraldehyde oxidised, a result borne out by the fact that, as already shown, the hydroxyaldehyde is the main product of the reaction.

The volatile acid products obtained by distillation of the original solution (calculated from the quantities of furfuraldehyde oxidised) amounted to

Formic	acid	 20-25	per cent.
Acetic	,,	 10—12	- "

It is not clear what proportion of these acids is formed in the original reaction, as the distillation is attended with "destruction" of the hydroxyfurfuraldehyde, and some part may be produced by this secondary decomposition. It is noteworthy that the yield of acetic acid is not affected by previously oxidising the neutralised solution with permanganate, and that very little oxalic acid is produced in this oxidation.

Methylated Products of Reaction.—We have alluded to the formation of methyl derivatives in the interaction of the peroxide and furfuraldehyde. Taking the yield of iodoform as an index of the quantity formed, the following results (I and II) were obtained in two experi-

ments carried out at 40° , as already described. The quantity is largely increased by allowing the interaction to proceed slowly at the ordinary temperature, that given in III being obtained in an experiment extending over 3 days:

I. 0.0716 CHI₂ per gram furfuraldehyde oxidised.

It is sufficiently clear from these numbers, together with those for acetic acid, that the hydrogen of the peroxide plays an important part, whether directly or indirectly, in the attack on the furfuran ring. We noted a similar phenomenon in studying the action of the peroxide upon the normal saturated carbohydrates, but the proportion of methylated products formed was relatively small.

Benzene and Hydrogen Peroxide.—As a confirmation of the main result of this investigation, it was thought expedient to examine the mode of interaction of the peroxide and typical aromatic compounds. Mr. Fenton called our attention to a paper by Martinon (Bull. Soc. Chim., 1885, [ii], 43, 156) on the interaction of phenol and the peroxide in presence of iron salts, the main product being catechol. Benzene appears also to have been superficially investigated, but in view of the conflicting evidence available (compare Houzeau and Renard, Compt. rend., 1873, 76, 572; Nencki and Giacosa, Zeit. physiol. Chem., 1880, 4, 339; Leeds, Ber., 1881, 14, 975; Nencki, ibid., 1144; J. pr. Chem. 1881, [ii], 23, 196), and the absence of systematic quantitative determinations, Mr. F. S. Young, M.A., is studying the oxidation of the hydrocarbon with hydrogen peroxide under the conditions obtaining in our experiments, and finds that phenol is formed as the first product (Proc., 1899, 15, 131). This result definitely confirms our conclusion that the introduction of hydroxyl groups into the furfuran ring is an indirect result, and is not due to the direct addition of OH-groups, which might be expected if the formula HO·OH represented the constitution of the peroxide.

Monohydroxyfurfuraldehyde.—The isolation of hydroxyfurfuraldehyde has not been achieved, although highly characteristic derivatives have been obtained. This failure is explained by the properties of the compound: thus, it is rapidly 'condensed' on heating the solution in which it is formed, it can be volatilised only in minute quantity by distillation of its aqueous solution at 50° under reduced pressure, ether extracts it only in fractional proportion from its aqueous solution, it is not precipitated by basic lead acetate, and an insoluble compound has not yet been found from which it can be recovered unchanged. Hydroxyfurfuraldehyde is precipitated by gelatin, and the product can be obtained in a striking manner by carrying out the

oxidation in presence of the substance; the voluminous precipitate thus formed contains 5.3 per cent. of nitrogen representing about 30 per cent. of its weight of gelatin in combination, and its production makes it probable that the OH-radicle is phenolic in character. Being so difficult of isolation, it is probable that hydroxyfurfuraldehyde has been overlooked in many reactions in which it may have been formed. Its identification as a constituent of the lignocelluloses is an indication of its wide distribution, and must further enlarge our views of the chemical problems involved in lignification. The proof of the presence of the hydroxyaldehyde itself or a closely related residue in the substance of lignified tissues rests on the following observations of the colour reactions previously described.

The solution obtained by the interaction of furfuraldehyde and hydrogen peroxide is mixed with a solution of phloroglucinol or resorcinol, hydrochloric acid is added until the colour begins to develop, and some form of cellulose fabric—cotton cloth, or filter paper is introduced. The cellulose is dyed with the product of condensation and the brilliant colours produced, purple and blue respectively, may be compared directly with the corresponding lignocellulose reactions developed on papers composed of "mechanical wood pulp." washing the coloured specimens in ordinary hard water, the brilliant colours are rapidly altered into dull shades, of brown and grey respectively, the change being easily shown to be due to a combination of the residual free OH-groups with the basic constituents of the water. The colour is restored on treatment with dilute acids, and the papers thus dved are found to be useful as indicators of acids and alkalis in solution. In all particulars, the colour reactions of this hydroxyfurfuraldehyde closely resemble those of the lignocelluloses.

A second characteristic reaction of the lignocelluloses is the deep yellow coloration produced in contact with solutions of aniline salts. It is easy to demonstrate that this property depends on a second and independent reactive group. The coloration which marks it is not affected by washing in water, and therefore, when both colouring matters are developed by successive treatment in solutions of phloroglucinol and the aniline salt, the mixed shade gives place on washing to the yellow of the aniline reaction, and is restored on treatment with a dilute acid.

A renewed study of the products of the acid hydrolysis of the lignocelluloses, in the light of these observations, has enabled us to effect a satisfactory resolution of the mixture, and an account of these investigations will be communicated at an early date. Moreover, we have been able to throw light on some still obscure relationships in the complex group of carbohydrates yielding furfuraldehyde and their oxidised products, particularly in regard to their condensations.

whether in the plant or by treatment with dehydrating agents. It is evident that the furfuraldehyde separated by distillation does not account for the total production of furfuran derivatives, since the hydroxy-derivative described in this paper would not accompany the furfuraldehyde, but would undergo decomposition during the reaction. It would seem, also, that the reaction of the pentoses themselves with phloroglucinol is due to hydroxyfurfuraldehyde formed in the process of condensation, and this also may in part account for the constant deficit of furfuraldehyde from the theoretical amount (64 per cent.) required by the equation

$$C_5H_{10}O_5 - 3H_2O = C_5H_4O_2$$
.

It is also well known that many oxy-derivatives of the hexoses, such as the glucosones and glycuronic acid, give relatively small yields of furfuraldehyde, although there is every reason to expect a much larger proportion of furfuran groups, and obviously there are many points in this special field of work which may be usefully revised in view of the results of the present investigations.

We are indebted to Mr. F. S. Young, M.A., and to Mr. J. S. Remington, for their kind assistance in the experimental work; we also have pleasure in stating that we are indebted to the Committee of the Royal Society for placing at our disposal a grant of money from the Government Research Fund.

LXXII.—Active and Inactive Phenylalkyloxyacetic Acids.

By ALEX. McKenzie, M.A., D.Sc.

THE replacement of the alcoholic hydrogen in active malic, lactic, and tartaric acids by alkyl groups causes a striking increase of optical activity. The primary object of the following investigation was to ascertain the effect of a similar replacement in the much more highly active mandelic acid.

Schreiner's method for making inactive ethereal alkyloxy-salts (Annalen, 1879, 197, 12) has not as yet been successfully applied in the case of active compounds. Purdie and Williamson, for instance, found (Trans., 1896, 69, 819) that the alkyloxypropionates produced by the action at ordinary temperature of sodium ethoxide on active ethylic a-halogen propionates were inactive, and J. Wallace Walker informs me that he has had a similar experience in applying the same reaction to an active ethereal halogen phenylacetate.

To obtain the active etheric mandelic acids, I therefore employed the method of direct alkylation by means of silver oxide and an alkyl iodide which has been recently found to give satisfactory results in the cases of ethereal malates and tartrates (Trans., 1899, 75, 157). Preliminary experiments were made with inactive ethereal mandelates.

Of the phenylalkyloxyacetic acids described, two have been made previously, namely, the inactive methoxy-acid, by Meyer and Boner by the action of sodium methoxide on methylic phenylchloracetate, and the inactive ethoxy-acid, by Körner and Radziszewski, by treatment of phenylbromacetic acid with alcoholic potash.

Action of Silver Oxide and Isopropylic Iodide on Inactive Methylic Mandelate.

Isopropylic iodide was here used in preference to other alkyl iodides. Purdie and Lander having previously shown (Trans., 1898, 73, 296) its peculiar tendency to form alkyloxy-ethereal salts with silver malate and silver lactate.

Isopropylic iodide (7 grams) was added to a mixture of silver oxide (2.5 grams) and methylic mandelate (3.5 grams), and when the action, which was brisk, had been completed by heating on a water-bath, the mixture was diluted with benzene and drained. On evaporating the benzene, an ethereal oil was left which, after hydrolysis and acidification, yielded mandelic acid and an acid oil sparingly soluble in water, An analysis of the zinc salt of this oil gave 15.7 per cent. of zinc, the calculated numbers for zinc mandelate and zinc phenylisopropoxyacetate being 17.80 and 14.48 respectively.

This experiment therefore indicated that mandelic acid and phenylisopropoxyacetic acid were produced, and the analysis of the zinc salt of the oil showed that the latter had been incompletely washed from mandelic acid. That phenylisopropoxyacetic acid should be precipitated from its salts on addition of acid as an oil sparingly soluble in water accords with the observations of Meyer and Boner (Annalen, 1883, 220, 45) and of Körner and Radziszewski (Zeit. Chem., 1868, 143) on the lower homologous acids.

In the action just described, there was distinct evidence of the presence of water, and methylic phenylisopropoxyacetate may be assumed to be formed according to the equation $2\text{Ph}\cdot\text{CH}(O\text{H})\cdot\text{COOMe} + Ag_2O + 2C_8H_7I = 2\text{Ph}\cdot\text{CH}(OC_8H_7)\cdot\text{COOMe} + 2\text{AgI} + H_2O$, whilst some methylic mandelate remains unchanged.

Action of Silver Oxide and Ethylic Iodide on Inactive Ethylic Mandelate.

Inactive ethylic mandelate was prepared by the sulphuric acid method (E. Fischer and Speier, Ber., 1895, 28, 3254), and melted at 37°; the yield was over 80 per cent. of the theoretical. Michael and Jeanprêtre (Ber., 1892, 25, 1684) had previously prepared it by the silver salt method and give 34° as the melting point. The silver oxide used in this and in succeeding experiments was prepared by precipitation with barium hydroxide and dried below 100° until constant.

37.5 grams of ethylic mandelate (1 mol.) were dissolved in 129 grams of ethylic iodide (4 mols.), 96 grams of silver oxide (2 mols.) were added, and when the vigorous action ceased, the mixture was heated on a water-bath and then diluted with benzene. After draining off the yellowish-black residue, and distilling off the excess of benzene and ethylic iodide, 39 grams of a neutral ethereal oil were obtained which did not crystallise in a freezing mixture, even after the addition of a nucleus of ethylic mandelate. This oil was hydrolysed with alcoholic potassium hydroxide, and when the alcohol had been expelled from the feebly alkaline solution, 24 grams of a yellowish, viscid oil were isolated by acidification and extraction with ether. The oil, which was further washed with water, was shown by analyses of its silver salt to be phenylethoxyacetic acid.

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0.4148 gave 0.6332 CO<sub>2</sub>, 0.1506 H<sub>2</sub>O, and 0.1564 Ag. C = 41.63; H = 4.03; Ag = 37.70.
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 $C_{10}H_{11}O_8Ag$ requires $C=41\cdot81$; $H=3\cdot83$; $Ag=37\cdot63$ per cent.

From a portion of the acid, a crystalline zinc salt, $C_{20}H_{22}O_6Zn + 3H_2O$, was prepared; this appeared to decompose above 105° .

```
0.7784 lost 0.0887 H_2O at 100—105° and gave 0.1369 ZnO. C_{20}H_{22}O_6Zn + 3H_2O requires H_2O = 11.31 per cent. Found H_2O = 11.39. C_{20}H_{22}O_6Zn requires Zn = 15.45 per cent. Found Zn = 15.94.
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The barium salt, $C_{20}H_{22}O_6Ba + 3H_2O$, crystallised in long needles grouped in rosettes, and was analysed.

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0.7057 lost 0.0711 H_2O at 120° and gave 0.2979 BaSO_4. C_{20}H_{23}O_6Ba + 3H_2O requires,H_2O = 9.84 percent. Found H_2O = 10.08. C_{20}H_{22}O_6Ba requires Ba = 27.68 per cent. Found Ba = 27.60.
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The salts obtained by Körner and Radziszewski (loc. cit.) were amorphous with the exception of the lead salt.

The next experiment was made to discover whether, under the observed conditions, the whole of the ethylic mandelate was converted into alkyloxy-salt. For this purpose, the action was conducted as

previously described, and the product (27 grams from 25 grams of the mandelate) was distilled under diminished pressure, giving 24 grams of a clear oil boiling at 143—145° under 15 mm. pressure; analyses showed it to consist of a mixture of the two ethereal salts.

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0.2681 gave 0.6763 CO<sub>2</sub> and 0.1867 H<sub>2</sub>O. C=68.80; H=7.74. 0.1711 ,, 0.4327 CO<sub>2</sub> ,, 0.1183 H<sub>2</sub>O. C=68.97; H=7.68. C_{10}H_{12}O_3 requires C=66.66; H=6.66 per cent. C_{12}H_{16}O_3 requires C=69.23; H=7.69 per cent.
```

These results indicate therefore that the product was the ethoxy-ethereal salt containing some mandelate, a conclusion which was confirmed by hydrolysing some of the oil and obtaining the crystalline mandelic acid, together with the oily ethoxy-acid. The experiment showed that fractional distillation was not a convenient method for separating ethylic phenylethoxyacetate from ethylic mandelate, and, by analogy, such would also be the case with the corresponding active compounds.

Action of Silver Oxide and Ethylic Iodide on Inactive Mandelic Acid.

In the previous experiments, there was evidence of the formation of water during the action. It appeared likely that the same products would be obtained by using the free acid instead of the ethereal salt, thus $Ph \cdot CHOH \cdot COOH + Ag_2O + 2EtI = Ph \cdot CHOEt \cdot COOEt + 2AgI + H_2O$. This was borne out by experiment. Silver oxide (2 mols.) was added to ethylic iodide (4 mols.) and mandelic acid (1 mol.), and, as before, a vigorous action started spontaneously. The treatment was similar to that previously described for the ethereal salt, and from 13 grams of the acid 9 grams of an oil were isolated, analyses of the silver salt of which gave 37.88 and 37.57 per cent. of silver, the calculated percentage for silver phenylethoxyacetate being 37.63.

In a second experiment, in the proportion of 1 mol. of oxide, 3 mols. of iodide, and 1 mol. of acid, the yield was much the same, and on extracting the acid after acidifying, mandelic acid was found to be present. The main product, either from the acid or the ethereal salt, is ethylic phenylethoxyacetate, with which is mixed some ethylic mandelate. The great difference in the solubility of phenylethoxyacetic and mandelic acids in water affords a ready means of separating the two, at any rate in the case of the inactive acids. Accordingly, levomandelic acid was used as the starting point for the preparation of the active phenylalkyloxyacetic acids to be subsequently described, the preliminary conversion into active ethereal salts being unnecessary.

Action of Silver Oxide and Ethylic Iodide on 1-Mandelic Acid.

The active mandelic acid used throughout was prepared from amygdalin (*Annalon*, 1848, 66, 238; *Ber.*, 1883, 16, 1565). A determination of the specific rotation of a sample, melting at 132—133°, gave the following result:

$$l=1$$
, $c=4.6903$, $\alpha_D^{20}=-7.42^\circ$, $[\alpha]_D=-158.2^\circ$.

Silver oxide (2 mols.) was added to a mixture of ethylic iodide (4 mols.) and l-mandelic acid (1 mol.), the action, which was vigorous, being conducted as in former experiments. On distilling off the benzene and ethylic iodide, the temperature finally rose rapidly from 100° to 150°, at which point the heating was stopped. From 22 grams of the acid, 29 grams of a neutral oil were obtained, from which the alkyloxy-acid was partially precipitated as a reddish oil after hydrolysis with potassium hydroxide solution and acidification with dilute sulphuric acid. The active ethoxy-acid was apparently more soluble in water than the inactive, for, were the solubilities about equal, a larger quantity of oil would, in this case, have separated. The acid, after extraction with ether, was dried in a vacuum and eventually the characteristic crystals of mandelic acid appeared in the Analyses of the silver salt of the product showed it to consist approximately of 74 per cent. of ethoxy-acid and 26 per cent. of mandelic acid. The complete separation of the two by the action of water was not so expeditiously effected as was at first expected, owing to the greater solubility of the active ethoxy-acid and the smaller solubility of the active mandelic acid in water as compared with the solubilities of the corresponding inactive acids. After being washed thrice with cold water, the oil was found, by analysis of its silver salt, to be incompletely freed from mandelic acid; it was accordingly further washed thrice with warm water, and as an analysis of the silver salt of the residual oil showed that the latter still contained some mandelic acid, it was finally purified by neutralisation with dilute ammonia and reprecipitation by dilute sulphuric acid. The oil, which subsided, was removed and washed four times with warm water, the last washings being found to contain neither sulphate nor mandelic Leevo-phenylethoxyacetic acid was obtained as a syrup after drying in a vacuum, and its purity was established by analysis of its silver salt.

^{0.3962} gave 0.6038 CO₂, 0.1405 H₂O, and 0.1490 Ag. C=41.56; H=3.94; Ag=37.61.

 $C_{10}H_{11}O_3Ag$ requires C=41.81; H=3.83; Ag=37.63 per cent.

The following polarimetric observations were made:

1-Phenylethoxyacetic acid.

	c.	N.	ŧ.	2.	a _D .	[a] _D .	[a] _D M/100'
Acid. (in acetone). (M=180).	3·7988 2·9932	0·21 0·17	15° 15	2 2	- 6·89° 5·30	- 90·8° 88·5	- 168·4° 159·8
Sodium salt. (M = 202).	10.6320 8.4365 3.3746 1.6878	0.53 0.42 0.17 0.08	12 12 12 12	1 1 1 2	8·74 6·94 2·68 2·59	82·2 82·3 79·4 76·8	166·1 166·3 160·4 155·1
Barium salt. $(\mathbf{M} = \frac{495}{2}).$	18:545 6:805 5:418 2:709	0.55 0.25 0.22 0.11	14 17 14 14	2 2 2 2	19·16 8·58 7·29 8·60	70·7 67·6 67·3 66·4	175·0 167·3 166·6 164·3

The concentrations of the acid were determined by titration against standard sodium hydroxide. The sodium and barium salts are both crystalline, and the concentrations of their solutions were found by estimating the metal in the residue obtained by evaporating known volumes to dryness and heating until anhydrous. The more dilute solutions were made from the more concentrated by suitable dilution. The letter N signifies normal; the numbers refer to the anhydrous compounds. The salts were analysed with the following results:

0.3370 anhydrous sodium salt gave 0.1201 Na_2SO_4 ; Na = 11.54. $C_{10}H_{11}O_2Na$ requires Na = 11.39 per cent.

0.4355 air dried barium salt lost 0.0406 H₂O at 130°, and gave 0.1574 BaCO₂.

 $C_{20}H_{22}O_6Ba + 3H_2O$ requires 9.84 per cent. Found $H_2O = 9.32$. $C_{20}H_{22}O_6Ba$ requires 27.68 per cent. Found Ba = 27.72.

Lavo-sthylic Phenylethoxyacetate.

As this substance cannot readily be prepared free from mandelate by the direct action of silver oxide on ethylic iodide and mandelic acid, it was considered necessary first to isolate the alkyloxy-acid and then to obtain the ethereal salt from this by the silver salt method. As the quantity of alkyloxy-acid at my disposal was rather small for this purpose, a fresh amount was made, with modifications having a bearing on the partial racemisation which, it will be shown, occurred in the preparation of the ethereal salt.

Silver oxide and I-mandelic acid, in molecular proportion, were used

and the action with ethylic iodide was more vigorous than in the first preparation. The mixed acids were obtained as previously described, but as mandelic acid had crystallised from the syrup in considerable quantity, it was deemed advisable to treat the mixed acids with more oxide and iodide, but even after this the ethoxy-acid still contained a little mandelic acid, from which it was separated by washing thoroughly with water and precipitating from its ammonium salt as before. The acid was finally converted into silver salt, which was analysed.

0.3131 gave 0.4797 CO₂, 0.1156 H₂O, and 0.1182 Ag. C = 41.79; H = 4.09; Ag = 37.75.

 $C_{10}H_{11}O_8Ag$ requires C = 41.81; H = 3.83; Ag = 37.63 per cent.

Dried L-silver phenylethoxyacetate (24 grams) was gradually added to an excess of ethylic iodide, and when the brisk action had ceased, the mixture was heated on the water-bath for an hour, diluted with anhydrous ether, and filtered. After removal of ether and ethylic iodide, the resulting oil was distilled under diminished pressure, and a slightly coloured product was obtained which boiled at 153° under 25—30 mm. pressure; this was redistilled and boiled at 146—147° under 17—20 mm. pressure. The first portion, 12 grams, was still very slightly coloured, the second, 4 grams, being colourless. Analyses of the first fraction showed it to be almost pure ethylic phenylethoxyacetate.

I. 0·1527 gave 0·3885 CO_2 and 0·1117 H_2O . C = 69·39; H = 8·13. II. 0·1817 ,, 0·4617 CO_2 ,, 0·1326 H_2O . C = 69·30; H = 8·11. $C_{12}H_{16}O_3$ requires C = 69·23; H = 7·69 per cent.

The following observation of the specific rotation was made:

$$l=1, t=21.5^{\circ}, a_{D}=-33.71^{\circ}, d\ 21.5^{\circ}/4^{\circ}=1.0429, [a]_{D}=-32.32^{\circ}.$$

After an interval of seven weeks, the two fractions were mixed, and the rotations taken in a 1 dcm. tube at different temperatures.

$$a_{\rm D}^{-7} = -38.80^{\circ}, \ a_{\rm D}^{\circ} = -37.59^{\circ}, \ a_{\rm D}^{11} = -35.70^{\circ}, \ a_{\rm D}^{21.5} = -33.67^{\circ}, \ a_{\rm D}^{20} = -32.25^{\circ}, \ d\ 30^{\circ}/4^{\circ} = 1.0349, \ [a]_{\rm D} = -31.16^{\circ}.$$

Racemisation is sometimes induced in a substance by leaving it at the ordinary temperature, thus Wallach (Annalen, 1892, 270, 190) found that limonene monohydrochloride decreased in rotation from 39.5° to 6.2° after some weeks. The observations just described show that such had not happened in this case.

To ascertain whether racemisation had occurred in the preparation of the ethereal salt, 3 grams were hydrolysed by heating with an aqueous solution of barium hydroxide; after expulsion of the alcohol, the excess of barium hydroxide was removed by means of carbonic anhydride, and the resulting solution of barium salt evaporated to

about 50 c.c. The concentration was estimated in an aliquot portion, the salt being dried at 120° until constant. An estimation of barium in the anhydrous salt showed its purity.

0.5946 gave 0.2796 BaSO₄. Ba = 27.65; theory = 27.68 per cent.

The specific rotation was as follows:

$$l=2$$
, $c=5.946$, $a_{\rm D}^{\rm so}=-4.10^{\circ}$, $[a]_{\rm D}=-34.48^{\circ}$,

and was thus about half that of the pure active salt.

Schulze and Bosshard (Zeit. physiol. Chem., 1886, 10, 135) found that active leucine, which preserves its activity when heated with water at 180°, becomes inactive on being heated with baryta solution at a lower temperature; albuminoids, also, when heated with baryta, sometimes give inactive products. That the partial racemisation had been induced by such a cause in this case was improbable, as the acid obtained from the ethereal salt by hydrolysing with aqueous potassium hydroxide, acidifying, and extracting with ether, formed a sodium salt, of which the specific rotation for c = 8.859 was $[a]_{10}^{16} = -35.8^{\circ}$, the specific rotation of the pure salt for a similar concentration being -82.3° .

The partial racemisation observed must therefore be attributed either to the violence of the initial action with silver oxide, or to the distillation in a vacuum, or to both.

Action of Silver Oxide and Methylic Iodide on Inactive Mandelic Acid.

Methylic iodide (4 mols.) was added to a mixture of silver oxide (1 mol.) and mandelic acid (1 mol.). The mixture of ethereal salts obtained weighed 13.5 grams from 13 grams of acid, and from this the mixed acids were isolated as an oil which soon crystallised in a vacuum. A melting point determination showed that the crystals, which weighed 9.5 grams, were a mixture; they were therefore dissolved in water, and from the aqueous solution mandelic acid crystallised on standing. After neutralising the whole with sodium hydroxide and concentrating, Meyer and Boner's sparingly soluble inactive sodium phenylmethoxyacetate (loc. cit.), CoHoOsNa+2HoO, was obtained, from which inactive phenylmethoxyacetic acid was isolated by decom-The acid was position with sulphuric acid and extraction with ether. more soluble in water than the corresponding ethoxy-acid; it separated in plates, and when recrystallised from a mixture of benzene and light petroleum melted at 69°. Meyer and Boner gave the melting point as 71-72°.

Action of Silver Oxide and Methylic Iodide on 1-Mandelic Acid.

A mixture of silver oxide (2 mols.) and l-mandelic acid (1 mol.) was added to methylic iodide (6 mols.) in four instalments during an interval of two hours; the action started almost at once, and was so regulated by cooling that it never became violent. After the mixture had been heated on the water-bath for an hour to the boiling point of methylic iodide, it was diluted with anhydrous ether, filtered, and the ether and iodide distilled off below 100° . The neutral oil obtained from 31 grams of the acid weighed 33.5 grams, and gave the strong lesvorotation $a_D^{tf} = -306^{\circ}$ in a 1 dcm. tube. The hydrolysis with aqueous potassium hydroxide was conducted at the ordinary temperature, and the acid obtained was an oil from which the sparingly soluble sodium phenylmethoxyacetate, $C_9H_9O_8Na + 2H_2O$, was obtained on neutralising with sodium hydroxide. This, when drained and thoroughly washed with cold water, weighed 22 grams. Its specific rotation was as follows:

$$l=2$$
, $c=2.028$, $a_D^{14}=-4.21^\circ$, $[a]_D=-103.8^\circ$.
0.2028, dried at 130°, gave 0.0760 Na₂SO₄. Na=12.14.

 $C_aH_aO_aNa$ requires Na = 12.23 per cent.

From the mother liquor, a further crop of 5 grams was removed; this contained $2H_2O$ ($H_2O=16.07$ per cent.), and had the following specific rotation:

$$l=2$$
, $c=2.267$, $a_D^{18}=-4.62^\circ$, $[a]_D=-101.9^\circ$.

The 27 grams of sodium salt obtained were recrystallised from water; the close agreement of the rotations given on p. 762 with those just quoted indicate that the recrystallisation was unnecessary, and that the salt was completely separated from sodium *l*-mandelate.

The acid obtained from the final mother liquor was, as expected, a mixture of mandelic and phenylmethoxyacetic acids.

l-Phenylmethoxyacetic acid was obtained from the sodium salt, by acidification and extraction with ether, as an oil which crystallised when cooled in a freezing mixture. It crystallised beautifully from light petroleum in long, glassy needles, melted at 63—64°, and gave the following result on analysis:

0.1267 gave 0.3020 CO₂ and 0.0725
$$H_2O$$
. C=65.01; H=6.36. $C_9H_{10}O_3$ requires C=65.06; H=6.02 per cent.

The acid was dried over sulphuric acid until of constant weight, and a portion titrated against N/10 sodium hydroxide solution. One hundred parts of sodium hydroxide required $24\cdot15$ parts (calculated $24\cdot1$ parts) of acid for neutralisation.

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The silver salt is sparingly soluble in cold water, and contained 39.73 per cent. of silver, the calculated number being 39.56.

The following polarimetric observations were made:

1-Phenylmethoxyacetic acid.

1-I nenyimethoxyacette acia.							
	c.	N.	t.	l.	α _D .	[α] _D .	$[\alpha]_{n}\frac{M}{100}$
Acid. (in water) (M=166).	1·5686 1·1724 0·5862	0·09 0·07 0·03	13·5° 13·25 13·25	2 2 2	-5·20° 8·87 1·92	- 165·8° 165·9 163·8	- 275·2° 275·4 271·9
(in acetone).	0·8187 18·625	0.02	13·5 13·25	2 0·5	0·95 .8·78	151·4 128·1	251·8 212·6
	5·450 2·180 1·090	0·33 0·13 0·07	13·25 12·5 12·5	2 2 2	13·40 5·27 2·66	122·9 120·9 122·0	204·0 200·7 202·5
(in alcohol).	6.7656 2.7062 0.5412	0·41 0·16 0·03	13·5 13 13	2 2 2	20·30 8·18 1·63	150·0 151·1 150·6	249 250·8 250·0
Sodium salt. (M=188).	10·592 4·250 2·125	0.56 0.28 0.11	15 15 14	2 2 2	22·57 8·87 4·38	106·5 104·4 101·9	200·2 196·3 191·6
Polassium salt. (M=204).	9·2670 4·6335 3·7068 1·8584 0·7414	0·45 0·23 0·18 0·09 0·04	14.75 14.75 14.75 15 15	0.5 0.5 0.5 2	4·55 2·28 1·75 8·48 1·86	98·2 96·3 94·4 93·9 91·7	200:8 196:5 192:6 191:6 187:1
Calcium salt. $(M = \frac{370}{2}).$	0.2559 0.224	0.01	14·5 14·5	2 2	1·10 0·43	98·4 96·0	182·0 177·6
Strontium salt. $(\mathbf{M} = \frac{417 \cdot 5}{2}).$	1.818 0.909	0·09 0·04	18 18	2 2	3·80 1·62	90·8 89·1	189·1 185·6
Barium salt. $(\mathbf{M} = \frac{4 \cdot 0 \cdot 7}{2}).$	4·414 1·772 0·886	0·19 0·07 0·04	14·5 14·5 14·5	2 2 2	7·73 8·02 1·47	87·6 85·2 83·0	204.5 198.9 193.8
Zinc salt. $(\mathbf{M} = \frac{395}{2}).$	1.380 0.6902 0.532 0.266	0·07 0·03 0·03 0·01	15 13·75 15 13	2 2 2 2	8:27 1:58 1:15 0:53	122.9 114.5 108.1 99.6	242·7 226·1 213·5 196·7
Magnesium salt. $(M = \frac{354.5}{2}).$	8·1088 4·0544 3·2435 1·6217 0·6487	0.46 0.23 0.18 0.09 0.04	13·25 11·75 18·5 11·75 11·25	2 2 2 2 2	18·72 9·03 7·17 3·50 1·38	115·4 111·4 110·5 107·9 106·4	204·5 197·5 195·9 191·3 188·6

The concentrations of the salt solutions used in the preceding observations were determined, for the most part, as previously indicated for the salts of the ethoxy-acid. The concentrations for the

potassium salt were ascertained by neutralising a weighed quantity of the acid with the calculated amount of normal potassium hydroxide solution and making up to a definite volume, and for the acid itself by direct weighing.

Calcium 1-phenylmethoxyacetate, C₁₈H₁₈O₆Ca, crystallises in anhydrous, glassy prisms with truncated domes, and is very sparingly soluble in water.

0.2147 gave 0.0761 CaSO₄. Ca = 10.42; theory = 10.81 per cent.

The strontium salt, C₁₈H₁₈O₆Sr, is also very sparingly soluble in water, although more soluble than the calcium salt; it crystallises in prisms.

0.1818, dried at 130° , gave 0.0786 SrSO_{4} . Sr = 20.62; theory = 20.96.

The barium salt, $C_{18}H_{18}O_6Ba + H_2O$, is much more soluble than the strontium salt, and crystallises in glassy, hexagonal prisms. The inactive salt, according to Meyer and Boner, crystallises with $2H_2O$.

0.4836 lost 0.0193 at 140°. $H_2O=3.99$; theory = 3.71 per cent. 0.1772 anhydrous salt gave 0.0889 BaSO₄. Ba = 29.5; theory = 29.34.

The zinc salt, $C_{18}H_{18}O_6Zn + 2H_2O$, is very slightly soluble in cold water, and crystallises in octagonal plates.

0.615 lost 0.0479 at 140°. $H_2O = 7.79$; theory = 8.35 per cent. 0.266 anhydrous salt gave 0.0557 ZnO. Zn = 16.8; theory = 16.46.

The magnesium salt, like the potassium salt, is readily soluble in cold water.

0.8891, dried at 140° , gave 0.1088 MgO. Mg = 7.38; theory = 6.86.

Rise of temperature, as was to be expected, was found to affect the rotation of an aqueous solution of the acid in the same sense as dilution.

$$l=2$$
, $c=1.5686$, $a_D^{25}=-5.03^\circ$, $[a]_D^{25}=-160.3^\circ$.

This can be taken only as an approximate value, however, as the density of the solution was not determined.

In the preparation of the acid used in the preceding determinations, the temperature was purposely kept as low as possible to minimise the chance of racemisation; it was found that methylic *l*-phenylmethoxyacetate, prepared from the acid by the silver salt method, does not undergo partial racemisation at 100°, as, after being heated at 100° for 1½ hours and then hydrolysed, it gave a barium salt, the specific rotation of which was as follows:

$$l=2$$
, $c=3.197$, $a_{D}^{13}=-5.52^{\circ}$, $[a]_{D}=-86.3^{\circ}$,

a value in close agreement with those previously quoted.

Action of Silver Oxide and Propylic Iodide on 1-Mandelic Acid.

A mixture of 64 grams of silver oxide (11 mols.) and 28 grams of l-mandelic acid (1 mol.) was added in four instalments during an interval of 2 hours to 150 grams of propylic iodide (5 mols.); the action was never violent, and was conducted in the manner previously The main portion of the excess of propylic iodide was distilled off along with ether from the product, but, on the temperature rising to 130°, the heating was stopped. The yield of neutral oil indicated the presence of propylic iodide which, during the subsequent hydrolysis with potassium hydroxide, would be decomposed into propylene. On acidifying the potassium salt, an oil was obtained as before; this was washed thrice with hot water, and a portion was then converted into silver salt, analyses of which gave 36:22 and 36 per cent. of silver respectively, the calculated percentage for silver phenylpropoxyacetate being 35.88, and thus indicated the possible presence of a little mandelic acid. After the oil had been dried in a vacuum until of constant weight, it was dissolved in benzene and an excess of light petroleum added; the alkyloxy-acid remained in solution, whilst the small quantity of mandelic acid present was precipitated, and recognised by titration against standard alkali. the benzene and light petroleum had been expelled from the solution, the alkyloxy-acid was again washed with water, from which it appeared that the acid was the most insoluble of the alkyloxy-acids hitherto described; the oil was dried in a vacuum until of constant weight, and its purity determined by titration. The yield amounted to 12 grams.

3.4048 required for neutralisation the calculated quantity, that is 17.35 c.c. of normal potassium hydroxide.

An analysis of the silver salt was also made.

0.3765 gave 0.1342 Ag. Ag = 35.64. $C_{11}H_{18}O_{3}Ag$ requires Ag = 35.88 per cent.

Solutions of the acid in acetone and of the potassium and barium salts in water were quite inactive.

Action of Silver Oxide and Isopropylic Iodide on 1-Mandelic Acid.

A mixture of 50 grams of silver oxide (1½ mols.) and 22 grams of l-mandelic acid (1 mol.) was added in six instalments during an interval of 2 hours to 98 grams of isopropylic iodide (4 mols.). The action started at ordinary temperature more quickly than with propylic iodide, and the boiling point of the iodide was soon reached, although at no time was the action permitted to become violent. After the

excess of ether and iodide had been distilled off under diminished pressure, first at ordinary temperature and then at 50° , 29 grams of an acid oil were obtained, which in a 1 dcm. tube had the rotation $a_D^{17} = -83^{\circ}5^{\circ}$. After further treatment in the customary manner, the reddish, oily product was completely separated from mandelic acid by treatment with water, then with a mixture of benzene and light petroleum, then by solution in ammonia and precipitation by dilute sulphuric acid, and finally by washing with hot water until free from sulphuric acid. When left for some time in a vacuum, the oil crystallised in characteristic prisms, differing in appearance from mandelic acid; from light petroleum, it separated as an almost colourless solid, and melted at $53-57^{\circ}$, which seemed to indicate the presence of some inactive acid. It was analysed by titration against standard alkali.

0.7039 required 36.35 c.c. N/10 sodium hydroxide for complete neutralisation. Calculated, 36.30 c.c.

The rotation of the acid was taken in acetone, in which it dissolves readily in the cold.

$$l=1$$
, $a=3.748$, $a_{D}^{18}=-3.18^{\circ}$, $[a]_{D}=-84.8^{\circ}$.

The sodium salt was made by exact neutralisation of the acid, and the following polarimetric observations were made:

$$l=2$$
, $c=2.066$, $a_D^{18.5}=-2.77^\circ$, $[a]_D=-67.0^\circ$. $l=2$, $c=0.8264$, $a_D^{18.5}=-1.08^\circ$, $[a]_D=-65.3^\circ$.

0.2066 anhydrous salt gave 0.0686 Na_eSO₄. Na = 10.76; theory = 10.65.

The potassium salt had the following specific rotation:

$$l=2$$
, $c=1.962$, $a_D^{15}=-2.43^\circ$, $[a]_D=-61.9^\circ$.

Conclusions.

Several experiments were tried with the view of throwing some light upon the mechanism of the silver oxide action, which has been applied in the preceding work. That silver oxide acts simply by removing hydrogen iodide from the sphere of action is improbable, as other oxides, like lead oxide and zinc oxide, yield no alkyloxy-salt. Purdie and Pitkeathly, however, have found that when mercuric oxide is heated with ethylic malate and ethylic iodide, the rotation of the product is considerably higher than that of the malate (Trans., 1899, 75, 157). The most plausible hypothesis is that an unstable silver compound is formed by replacement of the alcoholic hydrogen by silver, although, according to this view, cuprous oxide might be expected to have a similar effect.

Attempts to form ethylic phenylethoxyacetate by the action of sodium ethoxide on ethylic iodide and ethylic mandelate gave negative results.

I am inclined to the view that the formation of the ethereal alkyloxysalt is connected with the presence of water. It has been shown by Purdie and Lander (Trans., 1898, 78, 287) that when ethylic iodide, for example, acts on silver lactate, a mixture of ethylic lactate and ethoxypropionate is produced; and in every interaction of an alkyl iodide with silver malate or lactate examined by them, the presence of ethereal alkyloxy-salt could be demonstrated. Purdie and Pitkeathly (loc. cit.) have also explained the abnormally high rotations found by Rodger and Brame (Trans., 1898, 73, 301) for the ethereal tartrates prepared by the silver salt method as due to the presence of the highly active dialkyloxysuccinates. No such formation of ethereal alkyloxysalt, however, occurs when dry ethylic iodide acts on dry silver mandelate, the reaction taking place normally with formation of ethylic mandelate and silver iodide. There is evidence, although not at all marked, of the formation of the alkyloxy-compound when water is present, as the following experiment shows. 40 grams of dry silver mandelate were mixed with 97 grams of ethylic iodide and 5 c.c. of water, and after hydrolysis of the ethereal salt, and decomposition of the resulting potassium salt with acid, a little oil separated, but the quantity was so small that it was impossible to free it from mandelic acid and identify it by analysis as phenylethoxyacetic acid.

The replacement of the alcoholic hydrogen in *l*-mandelic acid by an alkyl group has not the same effect on optical activity as a similar replacement in aliphatic hydroxy-acids; in fact, in the case of *l*-phenylmethoxyacetic acid only is the specific rotation slightly higher than that of mandelic acid for similar concentrations, whilst with the ethoxy-and isopropoxy-acids the rotation was found to be considerably below that of mandelic acid. In the acids and salts examined, the specific rotation decreases with increasing weight in the alkyl group.

The rotations of the salts of l-phenylmethoxyacetic acid decrease with increasing dilution, and tend towards a minimum molecular rotation of 187°. Several of the rotations were taken in very dilute solutions, in which cases the experimental error in the molecular rotation, with the polarimeter used, amounts possibly to several degrees; accordingly, for the most dilute solutions, the values given for the molecular rotations must be regarded as only approximate. The effect of temperature, within the limits between which the various solutions were examined, is slight.

With regard to the rotation of the acid itself, the molecular rotation in alcohol remains constant with dilution, whilst in acetone it falls to a value comparable with that of the salts in water. The

molecular rotation in water, which is higher than that of the salts in water, falls with dilution, but with the most dilute solution the minimum is not nearly reached. The high figures obtained for the more concentrated aqueous solutions are not to be explained by the formation of an anhydride (which has always the effect of raising the rotation) as the acid is monobasic. With polybasic acids, on the other hand, as van't Hoff points out, the formation of a cyclic compound is possible, and the anomalous rotations of barium d-methoxysuccinate, which in concentrated solutions is lævorotatory but changes sign on dilution, may, for instance, be referred to this cause.

The rotations of aqueous solutions of the acid and its salts testify to the validity of the Landolt-Oudemans law and the results are clear in the light of the electrolytic dissociation theory. A marked connection between the amount of dissociation and rotation of an optically active electrolyte has been shown by Walden (Zeit. physikal. Chem., 1894, 15, 196) with a-bromocamphorsulphonic acid and its salts, and by Rimbach (loc. cit., 1895, 16, 671) with rubidium tartrate. Walden finds that the molecular rotation of a-bromocamphorsulphonic acid, which for v=30 is dissociated to the extent of over 90 per cent., falls with dilution and becomes constant when the degree of dissociation is above 94 per cent., the ion in this case rotating less strongly than the undissociated molecule. The salts also reach a minimum value. The optical rotation of electrolytes, however, in several cases appears to be dependent on some other factor than the number of active ions.

For the following determination of the affinity constant of *l*-phenylmethoxyacetic acid, I am indebted to Dr. Walther Roth, Assistant in the Second Chemical Institute, Berlin.

	K				
c.	$oldsymbol{v}_{oldsymbol{\cdot}}$	$(Hg = 10^7)$.	λ	λ•/λ ∞.	$(=100 \ \kappa).$
1.5686	10.59	2.744	29.06	0.0830	0.0709
0.3137	52.95	1.191	63.06	0.1802	0.0748

If the number of atoms in the molecule of the acid under investigation exceeds 12, λ_{∞} is dependent on it and independent of the nature of the acid (Ostwald, *Lehrbuch*, 2, 681); thus for orthacetamidobenzoic acid, the molecule of which contains the same number of atoms as

phenylmethoxyacetic acid,
$$\lambda_{\infty}$$
 is 350. The law $\left(\frac{\lambda_{v}}{\lambda_{\infty}}\right)^{2} / \left(1 - \frac{\lambda_{v}}{\lambda_{\infty}}\right)v$

 $=\kappa$ holds only for weak acids and for dilute solutions of the same. Ostwald does not generally determine the affinity constant in solutions stronger than v=32, so that, of the two determinations, 0.0748 should be taken as the more correct. This constant is intermediate between those for tartaric and mandelic acids, which are 0.097 and 0.042 respectively.

In the most dilute solution of which the rotation was taken, the acid is dissociated to the extent of only 18 per cent.

The degree of dissociation of an alkali salt of a monobasic acid is independent of the nature of the acid. The degree of dissociation of potassium phenylmethoxyacetate can be calculated from the molecular conductivity of other potassium salts, for instance, of the acetate. The most dilute solution used for the determination of specific rotation is about 1/27.5 normal. Now Kohlrausch (Ostwald, Lehrbuch, 2, 740) has measured the conductivity of 1/20 and 1/33.3 normal solutions of potassium acetate, and has found the values 82.0 and 84.1 respectively. The conductivity of 1/27.5 normal solution of potassium phenylmethoxyacetate will be about 83.1, the mean of these values, and as the average maximum conductivity of potassium acetate is 93.8, the degree of dissociation for the potassium methoxy-salt for c = 0.7414 is 83.1/93.8, that is, the salt is dissociated to the extent of about 90 per cent.

As the rotation of the acid and its salts falls with dilution, we may assume that the undissociated molecule rotates more strongly than the ion. The molecular rotation of the acid in equivalent concentration is accordingly higher than that of the salts which are dissociated to a greater degree. The molecular rotation of the acid would certainly fall with further dilution beyond c=0.3137, and approach the limit of the ionic molecular rotation.

Rimbach (Zeit. physikal. Chem., 1899, 28, 251) has recently determined with great exactitude the rotations of d-mandelic acid and sodium d-mandelate in very dilute solutions, and has found relationships similar to those described for l-phenylmethoxyacetic acid and its salts. The rotations fall with dilution, and the value $[a]_D = 143.7^{\circ}$ for the most dilute solution of the acid with c = 0.0583 (v = 261) showed that the minimum had not yet been reached, the ionic specific rotation deduced from the sodium salt determinations being about 100° .

With v = 256, mandelic acid is dissociated to the extent of 27.7 per cent. and sodium mandelate to that of 93 per cent..

It is remarkable that the rotation of *l*-phenylmethoxyacetic acid in acetone should correspond so closely with the rotations of the salts in water; such is also the case with the other acids examined. It may be supposed that the acid forms compounds with the solvent which in more dilute solution are rendered less complex until a limit is reached when the simplest compound is formed, the more complex the compound, the higher being the rotation. The fact that the rotation of the simplest compound approximates to that of the ion must be regarded as a coincidence.

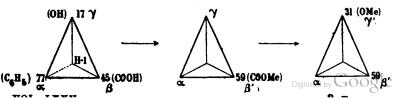
The ethoxy- and isopropoxy-acids and their salts present relationships similar to those described for the methoxy-acid. In the case of

the isopropoxy-acid, the value for molecular rotation would, doubtless, in more dilute acetone solution, approximate to those of the alkali salts in water.

The method of alkylating by means of silver oxide and alkyl iodide has been applied by Purdie and Pitkeathly (loc. cit.) for the preparation of active ethereal dialkyloxysuccinates, and by Purdie and Irvine (Trans., 1899, 75, 483) for that of active ethereal alkyloxypropionates, without any observation of partial racemisation during the process. The fact that by the action of silver oxide and an alkyl iodide on methylic and ethylic lactates active alkyloxypropionic acids have been prepared, and have practically the same rotations as those previously obtained by Purdie and Lander (Trans., 1898, 73, 862) by the resolution of the inactive alkyloxypropionic acids by morphine, is an indirect proof of the absence of racemisation in the preparation of the acids by the former method.

The racemisation phenomena occurring in the case of mandelic acid are therefore of interest. It is highly improbable that, in the preparation of the ethoxy-acid used for determinations of the specific rotation, the simple heating of the mixture of ethereal salts from 100° to 150° for a couple of minutes or so would cause racemisation to any considerable extent. It has been shown that, during the preparation of the ethylic salt from another specimen of active acid, partial racemisation had taken place. The other alkyloxy-acids were made with special precautions to avoid racemisation, so far, at any rate, as the latter is caused by rise of temperature, the initial actions being conducted gradually at the lowest possible temperatures, and never above the boiling points of the respective alkyl iodides. In the case of the methoxy-acid, the low temperature at which the action with silver oxide took place, the sharp melting point of the easily crystallisable product, and the non-racemisation of its methylic salt at 100° when heated for 11 hours, justify the supposition that no racemisation occurred in its preparation. The propoxy-acid was entirely inactive, the isopropoxy-acid active, but as the melting point of the latter was not sharp, it is doubtful if the full activity had been reached.

Besides the influence of heat in promoting the racemisation of an active body, another factor may, in special cases, be adduced, namely, that of weighting one of the groups. Take, for example, the case of the formation of methylic *l*-phenylmethoxyacetate from *l*-mandelic acid, methylic *l*-mandelate being regarded as first formed:



There is a certain attraction between the groups $a\beta$, which is less than that between $a\beta'$; when γ is replaced by γ' , we can imagine the weighting at this corner of the tetrahedron to still further increase the attraction between $a\beta'$. We must suppose that, with each replacement, the configuration of the tetrahedron changes, and that with the increase of weight from γ to γ' the change in figure is such that a approaches β' , and therefore the tendency to racemisation is increased. The temperature at which recemisation of an active substance begins will be definite for each substance, probably lower for methylic phenylmethoxyacetate than for methylic mandelate, and for methylic mandelate than for mandelic acid. In the formation of the ethylic ethoxy-salt from mandelic acid, β' and $\sqrt{\ }$ are increased from 59 and 31 to 73 and 45 respectively, and the tendency to racemisation is greater. In the formation of the propylic propoxy-salt, β' and γ' become 87 and 59, that is, whereas formerly a was greater than β' , now β' becomes greater than a, and with the change in configuration the tendency to racemisation should be increased.

These views were partly borne out by experiment, but cannot, of course, be generally applied. It is just as impossible for the case to be a general one as it is for us to imagine the asymmetric molecule of each active compound as possessing always the same definite structure, say, a regular tetrahedron.

Inactive phenylchloracetic acid was prepared by Easterfield by the action of hydrogen chloride on *l*-mandelic acid, and Walden has shown that this result was not due to the temperature employed, as active phenylchloracetic acid is obtained when phosphorus pentachloride is used at a higher temperature. The latter action, according to Walden (*J. Russ. phys. chem. Soc.*, 1898, 30, 632), is accompanied by the intermediate formation of labile compounds which undergo intramolecular change, and as the asymmetric carbon atom remains saturated, the product is active.

The inactivity of the phenylpropoxyacetic acid obtained may be ascribed partly to the relatively high temperature, 102°, at which the reaction with silver oxide was conducted and partly to the disruption of the asymmetric grouping in the formation of intermediate silver compounds. That the isopropoxy-acid was active is due, no doubt, to the lower temperature employed in its preparation and to the ease with which isopropylic iodide, in contradistinction to other alkyl iodides, replaces the alcoholic hydrogen of a hydroxy-acid.

My best thanks are due to Professors Purdie and Landolt, in whose laboratories this investigation was carried out.

United College of St. Salvator and St. Leonard, University of St. Andrews.

LXXIII.—Some Derivatives of Dimethyldihydroresorcinol.

By ARTHUR WILLIAM CROSSLEY.

A short time ago, Professor Perkin and the author (Trans., 1898, 73, 5, 23), by fusing camphoric acid with potash, obtained dihydrocamphoric acid, $C_{10}H_{18}O_4$, which, from its reactions and behaviour on oxidation, was thought to be most probably $aa_1\beta\beta$ -tetramethyladipic acid, $COOH\cdot CH(CH_8)\cdot C(CH_8)\cdot CH(CH_8)\cdot COOH$. The constitution of dihydrocamphoric acid is of great importance in assigning a formula to camphoric acid, and it was therefore decided to attempt the synthesis of this substituted adipic acid, in the hope that the two would prove to be identical.

The reaction of isobutylenic bromide and ethylic sodiomethylmalonate was first studied, in the hope that it might take place according to the following equation,

as from such a condensation product the tetramethyladipic acid could be obtained by hydrolysis and subsequent elimination of two molecular proportions of carbon dioxide. Although tried in alcohol, toluene, and xylene solution, and also in alcoholic solution under pressure, the ethylic methylmalonate was recovered unchanged, and only in toluene solution was any evidence of condensation observed, the product, however, being formed in much too small an amount for investigation. Further experiments in this direction were therefore abandoned.

It has been noticed by Bentley (Trans., 1895, 67, 266) and others that bromides containing a methyl group next to the carbon atom attached to bromine are of little use for synthetical work, as apparently hydrogen bromide is eliminated, which reacts with ethylic sodiomalonate, giving rise to sodium bromide and ethylic malonate; presumably, the reaction takes this course in the present case.

In order to see whether the unsymmetrical nature of the bromide exerted any influence, the action of ethylic sodiomethylmalonate on symmetrical butylenic bromide, CH₃·CHBr·CHBr·CH₈, was tried, but again condensation did not occur.

The next method which suggested itself was the interaction of mesityl oxide and ethylic sodiomalonate, in which it was expected that addition of the elements of the latter would take place at the double linking in the oxide. Unfortunately, the work of Vorländer on this

subject had been overlooked, as the reaction is not suited for the synthesis of the required substituted adipic acid. Vorländer (Annalen, 1897, 294, 253, 300) has shown that when mesityl oxide and ethylic sodiomalonate react in alcoholic solution, direct addition takes place at first, but loss of the elements of ethylic alcohol also occurs, giving rise to ethylic dimethyldihydroresorcylate, a substance which is easily converted into dimethyldihydroresorcinol by hydrolysis,

$$\underset{\mathrm{CH}_{3}}{\mathrm{CH}_{3}} > C \xrightarrow{\mathrm{CH}} \underset{\mathrm{CO}}{\overset{\mathrm{COOC}_{3}\mathrm{H}_{5}}{\overset{\mathrm{C}}{\overset{\mathrm{H}_{5}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{H}_{5}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{H}_{5}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}{\overset{\mathrm{C}}}}{\overset{\mathrm{C}}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}{\overset{C}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C}}}{\overset{C$$

After the publication of a short preliminary notice of my work (Proc., 1898, 14, 247), Dr. Vorländer called my attention to his research on the same subject, and further work with the substance was therefore abandoned (Proc., 1899, 15, 52). The following communication, giving a brief account of some derivatives of dimethyl-dihydroresorcinol not previously described, is published with the knowledge and consent of Dr. Vorländer, to whom I desire to tender my thanks both for his courtesy and for leaving in my hands the investigation of the interaction of ethylic sodiomethylmalonate and mesityl oxide, which is being continued in the hope that it may ultimately lead to the synthetical production of tetramethyladipic acid.

Vorländer (Annalen, 1898, 304, 15) has shown that when dimethyl-dihydroresorcinol is oxidised with alkaline permanganate at a tempera ture of 40—50°, the main product of the reaction is unsymmetrical dimethylsuccinic acid. Under these conditions, $\beta\beta$ -dimethylglutaric acid was not isolated, although its formation might reasonably be expected as a result of disruption of the ring at the positions indicated by the dotted lines.

$$\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_2}}{\sim}} \overset{\mathrm{CO}}{\sim} \overset{\mathrm{CH_2}}{\sim} \overset{\mathrm{CH_2}}{\sim} \overset{\mathrm{CO}}{\sim} \overset{\mathrm{CH_2}}{\sim} \overset{\mathrm{CO}}{\sim} \overset{\mathrm{CH_2}}{\sim} \overset{\mathrm{CO}}{\sim} \overset{\mathrm{CH_2}}{\sim} \overset{\mathrm{CO}}{\sim} \overset{\mathrm{CH_2}}{\sim} \overset{\mathrm{CO}}{\sim} \overset{\mathrm{CH_2}}{\sim} \overset{\mathrm{CH$$

and also in view of the fact that dihydroresorcinol, as Merling (Annalen, 1894, 278, 31) has shown, is readily oxidised by permanganate, yielding glutaric acid. The experiments described in this paper show that if dilute nitric acid, or a mixture of potassium dichromate and sulphuric acid, is substituted for potassium permanganate, there is no difficulty in isolating considerable amounts of $\beta\beta$ -dimethylglutaric acid.

EXPERIMENTAL.

Ethylic Dimethyldihydroresorcylate, (CH₃)₂C CH(COOEt)·CO CH₂, was prepared from ethylic sodiomalonate and mesityl oxide in a manner similar to that already described by Vorländer (Annalen, 1897, 294, 273, 300). It was first obtained as a thick, faintly yellow oil,

of which only a small amount passed over on distillation in a vacuum, the residue being transformed into a brilliant red resin, which has not been further examined. After a long time, the yellow oil solidified to a mass of colourless crystals melting at 76—78°, which after recrystallisation from a mixture of benzene and light petroleum separated in clusters of short, transparent, flattened needles melting at 78·5—79° (uncorr.). When heated above its melting point, the substance decomposes, evolves gas, and is transformed into the red resin.

$$\textit{Dimethyldihydroresorcinol}, (CH_8)_2 C < \begin{array}{c} CH_2 \\ CH_2 \end{array} \\ \begin{array}{c} CO \\ CH_2 \end{array} \\ \begin{array}{c}$$

Dimethyldihydroresorcinol was obtained from ethylic dimethyldihydroresorcylate in a manner differing but slightly from that employed by Vorländer (Annalen, 1897, 294, 314; 1898, 304, 18). The ethylic resorcylate was hydrolysed with alcoholic potash, and after adding water the alcohol was removed by evaporation. During this operation, a strong odour of peppermint was observed, and when the alkaline liquid was subsequently extracted with ether, a small amount of an oil having this characteristic odour was obtained; this substance partially solidified after long standing, but has not been further investigated.

The residual alkaline liquid, after acidifying with sulphuric acid, was extracted with ether, and the ethereal solution dried over calcium chloride; the solid residue obtained after evaporating the ether was purified by one or two recrystallisations from acetone, and analysed.

```
0.1458 gave 0.3674 CO_2 and 0.1124 H_2O. C = 68.72; H = 8.56. 0.1146 , 0.2876 CO_2 , 0.0884 H_2O. C = 68.44; H = 8.57. C_8H_{12}O_2 requires C = 68.57; H = 8.57 per cent.
```

On allowing the acetone mother liquors to slowly evaporate, a viscid residue was obtained, which probably contains the bye-products described by Vorländer (*Annalen*, 1898, 304, 17).

Dimethyldihydroresorcinol, the yield of which is from 70—75 per cent. of the theoretical, is insoluble in cold light petroleum and only slightly soluble on boiling; it dissolves in water, chloroform, ethylic acetate, benzene, or acetone on boiling, and separates on cooling in needle-shaped crystals; these melt at 148.5° (uncorr.), and at the same time give off a red liquid, which settles in the upper part of the capillary as a red film. When heated above its melting point, it is transformed into a red liquid, and on cooling sets to a hard, amber-like mass, which is completely soluble in alcohol, acetone, or aqueous potassium hydroxide (compare Merling, loc. cit.). Auric chloride and platinic

chloride do not precipitate a neutral solution of dimethyldihydroresorcinol in ammonia, but are reduced when the solutions are warmed.

I am indebted to Mr. W. J. Pope for kindly supplying the following crystallographic details:—

"The substance crystallises from acetone in large, transparent, monosymmetric prisms with a calcite-like lustre. The crystals are elongated in the direction of the axis b, and the form $a\{100\}$ is dominant; the forms in the zone [010] are well-developed, and usually striated parallel to the axis b. The forms $p\{110\}$ and $o\{121\}$ are small, but give good reflections on measurement; the pinacoid $b\{010\}$ is rarely present, and is always very small. The plane of symmetry is the optic axial plane, and a bisectrix of positive double refraction emerges through the face o(001); the angular dispersion is marked.

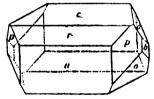
After melting on a microscope slide, the substance solidifies readily from centres in large individual flakes, frequently perpendicular to a bisectrix of negative double refraction,

"Crystalline system:—Monosymmetric,

$$a:b:c=1.3448:1:0.9433.$$

 $\beta=77^{\circ}17.5'.$

"Forms observed :— $a\{100\}$, $b\{010\}$, $c\{001\}$, $r\{101\}$, $p\{110\}$, and $c\{121\}$.



"The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean ob- served value.	Calculated value.
ap = 100: 110 pp = 110: 110 bp = 010: 110 ar = 100: 101 ac = 100: 001 ac = 100: 001 ac = 100: 110 po = 110: 121 ro = 101: 121 cp = 001: 121 oo = 121: 121 bo = 010: 121	42 18 6 25 87 16 21 44 25 27 19 19	52°23'— 53° 4' 74 17 — 74 58 37 5 — 37 21 46 7 46 51 30 16 — 81 0 76 59 — 77 81 102 26 — 103 4 65 12 — 65 82 34 19 — 35 1 79 38 — 80 5 81 58 — 82 56 66 31 — 67 0 60 54 — 61 22 83 29 — 34 9	52°41′ 74 84 87 15 46 82 80 89 5 77 14 102 47 65 24 84 48 79 52 82 24 66 48 61 7 33 48	74°38′ 37 19 46 38 77 17 5 102 42 5 34 48 79 48 82 20 66 42 61 10 38 41
oo = 12\overline{1}: 1\overline{2}\overline{1}\overline{1}\overline{1}: 1\overline{2}\overline{1}\overline{1}: 1\overline{2}\overline{1}\overline{1}: 1\overline{2}\overline{1}: 1\overline{1}: 11	12 18	118 16 —119 2 76 45 — 77 19	118 48 77 1 Digitized by	118 50 76 59 "

The silver salt, $C_8H_{11}O_2Ag$, was obtained by precipitating an accurately neutralised solution of dimethyldihydroresorcinol in ammonia with silver nitrate. It is a white, flocculent precipitate, and is somewhat readily soluble in hot water, separating, on cooling, in fine, grey, feathery needles.

· 0·3033 gave 0·4335 CO_2 , 0·1234 H_2O , and 0·1322 Ag. C = 38.97; H = 4.52; Ag = 43.58.

Additional silver determinations gave Ag = 43.89 and 43.97.

 $C_8H_{11}O_2Ag$ requires C=38.86; H=4.45; Ag=43.72 per cent.

The ethylic ether, $(CH_3)_3 \cdot C \xrightarrow{CH_2 \cdot C(OC_2H_5)} CH$, was prepared by heating the silver salt, suspended in dry ether, with the requisite amount of ethylic iodide in a reflux apparatus for 2 hours. The colourless oil, obtained after evaporation of the ether, and possessing a slight smell somewhat resembling that of celery, solidified to a mass of needle-shaped crystals, and was recrystallised from light petroleum (b. p. $40-60^\circ$).

0.1248 gave 0.3268 CO₂ and 0.1069 H₂O. C = 71.41; H = 9.51, $C_{10}H_{16}O_{2}$ requires C = 71.42; H = 9.52 per cent.

Determinations of the molecular weight by Raoult's method, using acetic acid as solvent, gave the following results:

Found, (I) 175, (II), 174; $C_{10}H_{16}O_2$ requires mol. wt, = 168,

The ether crystallises from light petroleum in stout, transparent, lustrous prisms, which are usually twinned and apparently belong to the monosymmetric system; it melts at $59.5-60^{\circ}$, distils without decomposition at 252° under the ordinary atmospheric pressure, and is readily soluble in cold acetone, chloroform, alcohol, or ether, but only sparingly so in cold light petroleum. When treated with alcoholic potash, it is converted quantitatively into dimethyldihydroresorcinol, melting at 148.5° as already described.

Bromodimethyldihydroresorcinol, $(CH_3)_2 \cdot CCH_2 \cdot C(OH) > CBr + H_2O_0$ —Dimethyldihydroresorcinol was dissolved in dry chloroform, and a solution of dry bromine in chloroform gradually added in the dark until the colour became permanent. As soon as this occurred, hydrogen bromide was evolved, and a white solid separated, which was collected, spread on a porous plate, and purified by recrystallisation from dilute alcohol. The crystals effloresce in a vacuum over sulphuric acid, and by this means the water of crystallisation in the air-dried salt was determined. In the second analysis, the substance was heated at 80° in an air-bath until a constant weight was attained,

- I. 0.5414 lost 0.0416 $H_2O = 7.68$. II. 0.5947 lost 0.0470 $H_2O = 7.90$. $C_8H_{11}O_2Br + H_2O$ requires $H_2O = 7.59$ per cent.
- Bromine determinations in the anhydrous substance gave the following numbers:
 - I. 0.2714 gave 0.2346 AgBr. Br = 36.78. II. 0.2306 gave 0.1997 AgBr. Br = 36.84.

 $C_8H_{11}O_8Br$ requires Br = 36.53 per cent.

Bromodimethyldihydroresorcinol is insoluble in light petroleum or chloroform, slightly soluble in toluene, and readily so in alcohol, acetone, or acetic acid. It crystallises best from dilute alcohol in white, glistening leaflets, or after repeated crystallisation in long, needle-shaped crystals containing 1H₂O, and melting with slight decomposition at 173—173·5° (uncorr.). The dried substance melts, decomposes, and gives off gas at 143—144°.

When dissolved in dilute aqueous potassium hydroxide and treated with sodium amalgam, it is converted quantitatively into dimethyldihydroresorcinol, behaving in this respect like dihydroresorcinol (Merling, loc. cit.). Alcoholic potash, however, seems to have little or no action on it, as potassium bromide did not separate after it had been heated for $4\frac{1}{2}$ hours on a water-bath with twice its weight of potassium hydroxide dissolved in alcohol, and on acidifying and extracting with ether, bromodimethyldihydroresorcinol was recovered in nearly theoretical amount.

 $Bromodimsthyltstrahydroresorcinol, (CH_3)_2 \cdot C < \begin{array}{c} CH_2 \cdot & -CO \\ OH_3 \cdot CH(OH) \end{array} > CHBr.$

—Dimethyldihydroresorcinol was dissolved in glacial acetic acid previously saturated with dry hydrogen bromide, and after some time beautiful, transparent crystals separated. The excess of acetic acid containing hydrogen bromide was poured off, and the crystals were rapidly and repeatedly washed by decantation with cold acetone, dried in a vacuum, and analysed.

0.1638 gave 0.1391 AgBr. Br = 36.14. C₈H₁₃O₂Br requires Br = 36.20 per cent.

This substance crystallises from an acetic acid solution of hydrogen bromide in large, transparent, rhombic plates, which melt at 168—169° with decomposition and evolution of gas. It deliquesces rapidly on exposure to the air, is insoluble in cold acetone, light petroleum, or chloroform, and soluble in hot alcohol or acetone, but could only be obtained crystalline in the manner just described. When treated with alcoholic potash or with sodium amalgam, it is reconverted into dimethyldihydroresorcinol.

Oxidation of Dimethyldihydroresorcinol.

Oxidation with Dilute Nitric Acid.—Dimethyldihydroresorcinol was boiled with ten times its weight of nitric acid of sp. gr. 1.15 in a reflux apparatus. The mixture gradually changed in colour, and after about 15 minutes became a deep cherry red, and the oxidation violent; when the vigorous reaction had subsided, the heating was continued for about half an hour to complete the oxidation. The excess of nitric acid was removed by evaporation on a water-bath, and after treating repeatedly with water to ensure the removal of all but the last traces of nitric acid, the residue solidified to a mass of crystals. These were spread on a porous plate, dissolved in water, neutralised with ammonia, and boiled with excess of calcium chloride solution. After removing the precipitate, which gave off carbon monoxide on heating with concentrated sulphuric acid, the filtrate was evaporated to a small bulk, acidified with hydrochloric acid, and extracted repeatedly with pure ether, the ethereal solution being dried over calcium chloride and the ether evaporated. The solid residue was then heated with acetic chloride for two hours, and after removal of the excess of the solvent by evaporation, the product soon solidified as a mass of glistening plates, which, although repeatedly recrystallised from petroleum boiling at 100-120°, did not melt sharply. The crystals dissolved for the most part readily in cold benzene, and after filtering from a small amount of insoluble material and allowing the solution to evaporate spontaneously, long, flat needles separated which melted at 124-125° and gave the following numbers on analysis.

0.1094 gave 0.2372 CO₂ and 0.0702 H₂O. C = 59.13; H = 7.13. $C_7H_{10}O_8$ requires C = 59.15; H = 7.04 per cent.

The substance had all the properties ascribed to $\beta\beta$ -dimethylglutaric anhydride by Perkin and Goodwin (Trans., 1896, 69, 1475), and was characterised by converting it, by boiling with water, into the corresponding acid melting at 100—101°, into the anilic acid melting at 134—135°, and into the anil melting at 158° (compare Perkin and Goodwin, loc. cit.).

In a second oxidation, the product, after removal of the nitric acid by evaporation, was treated directly with acetic chloride, with exactly similar results.

Oxidation with Potassium Dichromate and Sulphuric Acid.—A solution of 16 grams of potassium dichromate in dilute sulphuric acid was gradually added to 5 grams of dimethyldihydroresorcinol dissolved in 100 c.c. of water, and the mixture heated for half an hour on the water-bath to complete the oxidation, which takes place very readily. The product was isolated by removing the chromium by

precipitation with sodium carbonate, evaporating the filtrate to a small bulk, acidifying with hydrochloric acid, and extracting ten times with pure ether. The residue left after evaporating the ether solidified on cooling, and after drying on a porous plate was treated with acetic chloride exactly as described under the oxidation with nitric acid. The crystalline solid thus obtained melted at $124-125^\circ$, and was identified as $\beta\beta$ -dimethylglutaric anhydride by analysis,

0.1142 gave 0.247 CO₂ and 0.0722 H_2O . C=58.99; H=7.02. $C_7H_{10}O_3$ requires C=59.15; H=7.04 per cent.

and by conversion into the corresponding acid melting at 100-101°,

CHEMICAL LABORATORY, St. Thomas's Hospital,

LXXIV.—Condensation of Ethylic Salts of Acids of the Acetylene Series with Ketonic Compounds,

By SIEGFRIED RUHEMANN and A. V. CUNNINGTON,

As shown before (this vol., 245, 411), the ethylic salts of β -ketonic acids—for example, ethylic acetoacetate and ethylic benzoylacetate—condense with ethylic phenylpropiolate to a-pyrone derivatives under the influence of sodium ethoxide. The behaviour of β -diketones, such as acetylacetone and benzoylacetone, towards the ethylic salts of the unsaturated acid is similar, and leads to the formation of the corresponding cyclic compounds of the general formula;

$$C_6H_6 \cdot C < CH - CO \cdot R): CR' > 0.$$

We have undertaken the further study of the interaction of ethylic salts of acids of the acetylene series with those of β-ketonic acids, in order to ascertain whether they also yield a-pyrone derivatives, and find that, on using substitution products of ethylic phenylpropiolate and ketonic compounds of the types R·CO·CH₂·COOC₂H₅ or R·CO·CH₂·COO·R', such cyclic compounds are produced; the reaction, however, takes a different course if ethylic acetylenedicarboxylate is used instead of ethylic phenylpropiolate. The union of this salt with ethylic benzoylacetate is readily effected by means of sodium ethoxide; it is not accompanied, however, by the loss of alcohol and condensation to an a-pyrone compound. The product does not dissolve in alkali, does not give a colour reaction with ferric chloride, and does not condense with ammonia to a pyridine derivative.

These facts lead to the view that the reaction does not take place in the following manner:

$$\begin{aligned} \text{COOC}_2\mathbf{H}_5 \cdot \text{CiC} \cdot \text{COOC}_3\mathbf{H}_5 + \text{COOC}_2\mathbf{H}_5 \cdot \text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\mathbf{H}_5 = \\ \text{COOC}_2\mathbf{H}_5 \cdot \text{C}; \text{CH} \cdot \text{COOC}_2\mathbf{H}_5 \\ \text{COOC}_0\mathbf{H}_5 \cdot \text{CH} \cdot \text{CO} \cdot \text{C}_6\mathbf{H}_6 \end{aligned}$$

and indicate that both hydrogen atoms of the CH₂-group of the ketonic compound play a part in the union of the two ethylic salts. For the constitution of the additive compound, there remains a choice between the two formulæ:

Either of these formulæ would correspond with the above-mentioned behaviour, yet we are inclined to prefer formula II, which represents the substance as ethylic benzoyltrimethylenetricarboxylate, since, on treatment with alcoholic ammonia, a monamido-compound is produced, whilst, in the light of the researches on the action of ammonia on the ethylic salts of aconitic acid and its homologues, it would be expected that a compound of the constitution I would condense to a pyridine derivative.

We are at present engaged in the study of the acid which is obtained by the hydrolysis of the ethereal salt, with the object of confirming the conclusion as to its constitution derived from the above considerations.

One of the authors (loc. cit.) has shown that the a-pyrone compounds, which are produced by the condensation of ethylic phenylpropiolate with ethylic acetoacetate and ethylic benzoylacetate, can readily be changed into pyridine derivatives. This is effected by the substitution of the ethyl radicle for the ammonium group in the additive compounds of the a-pyrone derivatives with 2 mols. of ammonia, and distillation of the ethylic salts thus formed. These salts had not been isolated, and it is therefore of interest that such a compound can readily be obtained from the a-pyrone derivative which is produced by the condensation of benzoylacetone with ethylic phenylpropiolate. This salt, which is most probably to be represented by the formula,

loses alcohol on distillation in a vacuum, and is quantitatively transformed into the pyridine derivative.

It may further be pointed out that the a-pyrone compounds also form additive products with 2 mols. of primary bases, such as ethyl-

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amine. These we hope to be able to transform into derivatives of pyridine which contain an alkyl group united with the nitrogen atom.

The present paper contains, besides a record of the work indicated above, the description of some experiments on the behaviour of sodium ethoxide towards a mixture of ethylic phenylpropiolate and alkyl derivatives of ethylic acetoacetate. We found that the reaction was incomplete and that a mixture of substances was produced which we were unable to separate by fractional distillation.

Experimental.

$$\gamma$$
-Phonyl-a'-mothyl-a-pyrone, $C_6H_5 \cdot C \stackrel{CH}{\leftarrow} CO \rightarrow C$.

On adding a small quantity of sodium ethoxide (0.5 gram) to the mixture of ethylic phenylpropiolate and acetylacetone, an oil is obtained which, as mentioned before, yields ethylic γ -diaceto- β -phenylcrotonate and γ -phenyl-a'-methyl- β '-aceto-a-pyrone on distillation. The formation of the latter is, however, accompanied by that of ethylic acetate and γ -phenyl-a'-methyl-a-pyrone if the mixture is digested with an excess of sodium ethoxide (several grams) for one to two days on the waterbath. The separation is effected by adding dilute sulphuric acid to the product and submitting the oil thus precipitated to fractional distillation in a vacuum; phenylmethylaceto-a-pyrone passes over between 210° and 220° under about 12 mm. pressure, and γ -phenyl-a'-methyl-a-pyrone at 270—280°. The latter crystallises from alcohol in faintly yellow, prismatic plates which soften at 172° and melt at 180°.

0.2040 gave 0.5798 CO₂ and 0.0988 H₂O.
$$C = 77.51$$
; $H = 5.38$. $C_{12}H_{10}O_2$ requires $C = 77.41$; $H = 5.37$ per cent.

This compound owes its formation undoubtedly to the decomposition which the corresponding aceto-derivative undergoes under the influence of sodium ethoxide as expressed by the equation:

$$\begin{array}{c} C_{6}H_{5}\cdot C:CH\cdot CO\\ CH_{3}\cdot CO\cdot C:C(CH_{3}) \\ \hline \\ C_{6}H_{5}\cdot C:CH \\ \hline \\ CNa:C(CH_{3}) \\ \hline \\ \\ COOC_{2}H_{5}. \end{array}$$

Action of Ethylamine on Ethylic a'-Methyl-γ-phenyl-a-pyroneβ'-carboxylate.

Ethylamine, just like ammonia, yields additive products with a-pyrone derivatives. We have studied this reaction more particularly in the case of the compound which is formed by the condensation of ethylic phenylpropiolate and ethylic acetoacetate. The additive product

dissolves in alcoholic ethylamine and the solution does not deposit a solid after standing for two days; on evaporating the yellow solution under diminished pressure, a solid residue remains which almost completely dissolves in water containing a little ethylamine.

This compound is undoubtedly the ethylammonium salt, and is probably represented by the formula:

The aqueous solution yields, with silver nitrate, a yellowish precipitate of the corresponding silver salt, which, after washing with water and then with alcohol, is dried in a vacuum.

0.2680 left, on ignition, 0.0710 Ag.
$$Ag = 26.49$$
. $C_{17}H_{20}NO_4Ag$ requires $Ag = 26.34$ per cent.

We hope to transform this silver salt into the pyridine derivative containing the ethyl group united with the nitrogen.

$$\gamma a'$$
-Diphenyl- β' -acetyl-a-hydroxypyridine.

Benzoylacetone and ethylic phenylpropiolate, as shown by one of us (loc. cit.), under the influence of sodium ethoxide, condense to an a-pyrone derivative, which most probably is to be represented by the formula:

Its additive compound with 2 mols. of ammonia yields a silver salt of the formula $C_{19}H_{16}AgNO_3$ on treatment with silver nitrate. This, after drying in a vacuum, is digested with ethylic iodide on the waterbath for two hours; the excess of the iodide is evaporated and the residue extracted with boiling alcohol. The alcoholic filtrate from the silver iodide, on cooling, deposits faintly yellow plates, which melt at $161-162^\circ$, dissolve sparingly in cold, but readily in boiling alcohol, and are insoluble in alkali. This substance is the ethylic salt corresponding with the silver compound, and on analysis gave the following results:

0.2031 gave 0.5595
$$CO_2$$
 and 0.1157 H_2O . $C = 75.16$; $H = 6.33$. 0.3060 ,, 10.8 c.c. nitrogen at 14° and 776mm. $N = 4.23$. $C_{21}H_{21}NO_3$ requires $C = 75.22$; $H = 6.26$; $N = 4.22$ per cent.

From a consideration of the mode of transformation of a-pyrone compounds into pyridine derivatives (*loc. cit.*), the constitution of this substance is most probably expressed by the following formula:

$$\mathbf{C_6H_5 \cdot C} < \!\!\!\! < \!\!\!\! \stackrel{\mathbf{CH \cdot COOC_9H_5}}{\mathbf{C(COCH_8) : C(C_6H_6)NH_9}}.$$

This view explains also the change which the ethylic salt suffers when heated in a vacuum. It first melts, then ebullition takes place, accompanied by the formation of white clouds which indicate the elimination of alcohol, and at a temperature above 300° a yellowish oil distils without decomposition which at once solidifies. This dissolves readily in glacial acetic acid, but only sparingly in alcohol, and crystallises from the latter in colourless needles which melt at 225°.

Diphenylacetopyridone, $C_6H_5 \cdot C < CH - C(OO \cdot CH_8) \cdot C(C_6H_5) > N$, has acid properties, since it is soluble in dilute caustic potash, especially on warming, and is precipitated unchanged on the addition of a mineral acid to the alkaline solution; it is not dissolved in hydrochloric acid, however, and therefore does not exhibit the properties of a base.

0.2007 gave 0.5800 CO₂ and 0.0942 H₂O. C=78.81; H=5.21. 0.3192 ,, 13.5 c.e. nitrogen at 15° and 776 mm. N=5.05. $C_{19}H_{18}NO_2$ requires C=78.89; H=5.19; N=4.84 per cent.

Formation of a-Pyrone Compounds from Ethylic Paranitrophenylpropiolate and the Ethylic Salts of β-Ketonic Acids.

The ethylic salts of phenylpropiolic acid with substituents in the nucleus, as mentioned above, combine with those of acetoacetic and benzoylacetic acids, under the influence of sodium ethoxide, as readily as does ethylic phenylpropiolate itself. As an example of such a derivative, we have chosen ethylic paranitrophenylpropiolate.

Ethylic γ -Paranitrophenyl- β '-methyl-a-pyrone- β '-carboxylate,

$$NO_2 \cdot C_6H_4 \cdot C < CH \longrightarrow COOC_2H_5 > O$$

is produced by digesting equivalent quantities of ethylic paranitrophenylpropiolate and acetoacetate with 0.5 gram of sodium ethoxide on the water-bath for 3 hours; the dark product is acidified with dilute sulphuric acid and repeatedly extracted with ether.

The a-pyrone compound, being sparingly soluble in ether, separates from this solvent in yellowish prisms, which, when recrystallised from boiling alcohol, melt at 131—132°.

0.2330 gave 0.5070 CO₂ and 0.0895 H₂O. C=59.34; H=4.26. 0.3030 ,, 12.5 c.c. nitrogen at 17° and 762 mm. N=4.80. $C_{15}H_{13}NO_6$ requires C=59.40; H=4.29; N=4.62 per cent.

Ethylic γ-Paranitrophenyl-a'-phenyl-a-pyrone-β'-carboxylate,

$$NO_2 \cdot C_6H_4 \cdot C \stackrel{CH}{\underset{C(COOC_2H_5):C(C_6H_5)}{\longleftarrow}} O.$$

—This compound is obtained by mixing ethylic benzoylacetate (11 grams) with sodium ethoxide (0.5 gram), and then adding ethylic para-

nitrophenylpropiolate (12 grams). The mixture is warmed over a flame until it melts, and finally digested on the water-bath for 2 hours. The red product thus obtained is treated with dilute sulphuric acid and extracted with ether; the ethereal solution, on standing, deposits yellowish plates which dissolve sparingly in alcohol and melt at 150°.

0.2288 gave 0.5505 CO₂ and 0.0850 H₂O. C = 65.61; H = 4.12. 0.3270 , 11 c.c. nitrogen at 16° and 764 mm. N = 3.94. $C_{20}H_{16}NO_6$ requires C = 65.75; H = 4.11; N = 3.83 per cent.

Ethylic \(\gamma\)-Phenyl-a-pyrone-a'\(\beta'\)-dicarboxylate,

—The preparation of this substance from ethylic oxaloacetate and ethylic phenylpropiolate requires care, on account of the ease with which the ethylic salt of the ketonic acid decomposes. The method which in the former cases led to the formation of α-pyrone compounds cannot be used, since evolution of gas occurs on digesting the mixture of the two ethylic salts with sodium ethoxide.

The condensation, however, can be effected in the following manner. Ethylic exaloacetate is gradually mixed with an equivalent quantity of dry sodium ethoxide suspended in absolute ether, and ethylic phenylpropiolate is slowly added; the green solution thus produced, after standing for 2 to 3 days at the ordinary temperature, is treated with dilute sulphuric acid, and, after removal of the ether, yields a very viscous oil which does not deposit crystals, and decomposes on distillation in a vacuum. When digested with a small quantity of sodium ethoxide on the water-bath and then treated with dilute sulphuric acid, this product forms an oil which deposits crystals after some time; these are collected by the aid of a pump, and dissolved in ether. On allowing the ether to evaporate slowly, yellowish, prismatic plates separate which melt at 94—95°, are very soluble in alcohol, and are not decolorised by treatment with animal charcoal. The compound was dried in a vacuum and analysed.

0.1963 gave 0.4620 CO₂ and 0.0905 H₂O. C = 64.28; H = 5.12. $C_{17}H_{16}O_6$ requires C = 64.55; H = 5.06 per cent.

The yield is very small, and this circumstance prevented us from studying the a-pyrone compound further.

Action of Ethylic Phenylpropiolate on Ethylic Alkyl Acetoacetates in the presence of Sodium Ethoxide.

On examining the action of sodium ethoxide on a mixture of ethylic phenylpropiolate, and of β -diketones, or the ethylic salts of β -ketonic

acids, which contain the CH₂-group, it was found that the resulting oils, when distilled, yielded, besides α-pyrone derivatives, fractions with lower boiling points which probably consist of unsaturated ketonic compounds, forming the intermediate products of the reaction.

In one case, a substance of this type has been isolated (this vol., 415); this fact led to the view that the formation of the additive products preceded that of the pyrone derivative, and induced us to study the action of sodium ethoxide on a mixture of ethylic phenylpropiolate, and ethylic alkylacetoacetates, in the hope of preparing unsaturated ketonic compounds of the general formula,

$$C_6H_5 \cdot C : CH \cdot COOC_2H_5$$

 $CH_3 \cdot CO \cdot CR \cdot COOC_2H_5$

In using ethylic acetoacetate, the reaction proceeds with marked evolution of heat, but scarcely any rise of temperature is observed on adding 0.5 gram of sodium ethoxide to the mixture of the ethylic salt of the unsaturated acid and that of the alkylated acetoacetic acid. Our experiments led to the conclusion that the reaction is complicated whether the mixture is heated on the water-bath for a longer or a shorter time, or whether the relative amount of sodium ethoxide is increased or not. In all cases, oils are obtained which boil through wide ranges of temperature.

We have repeatedly tried to separate pure substances from the mixtures by fractional distillation, but in vain. In one instance only, namely, in using ethylic propylacetoacetate, have we been able to obtain a definite substance of the expected type from the product of the reaction; this boiled at 203—206° under 10 mm. pressure, and on analysis gave numbers agreeing with those required for the formula,

$$\begin{array}{c} \mathbf{C_6H_5 \cdot C \cdot CH \cdot COOC_2H_5} \\ \mathbf{CH_8 \cdot CO \cdot C(C_3H_7) \cdot COOC_2H_5} \end{array}$$

0.2345 gave 0.5975 CO_2 and 0.1595 H_2O . C = 69.49; H = 7.55. $C_{20}H_{26}O_5$ requires C = 69.36; H = 7.57 per cent.

Additive Compounds of Ethylic Salts of β-Ketonic Acids and Ethylic Acetylenedicarboxylats.

We have already mentioned in the introduction that, under the influence of sodium ethoxide, the action of ethylic salts of β -ketonic acids on ethylic acetylenedicarboxylate differs from that on ethylic phenylpropiolate, giving rise to compounds which most probably are to be considered as trimethylene derivatives. Since on adding dry sodium ethoxide to the mixture of the ethylic salts, the action is

accompanied by a great evolution of heat, we have modified the method by using absolute ether as diluent.

Tristhylic Benzoyltrimethylenetricarboxylate,

$$\underbrace{\text{COOC}_2\text{H}_5\text{·CH}}_{\text{COOC}_2\text{H}_5} \cdot \underbrace{\text{COOC}_2\text{H}_5}_{\text{CO·C}_6\text{H}_5}.$$

—Absolute ether, containing 3.4 grams of sodium ethoxide in suspension, is gradually mixed with 9.6 grams of ethylic benzoylacetate, and, when solution is effected, 8.5 grams of ethylic acetylenedicarboxylate are added; a reaction immediately sets in, and a yellow precipitate is formed. After standing for a day, the mixture is shaken with dilute sulphuric acid, when the solid dissolves and the colour disappears. The ethereal layer is separated, and after removal of the ether, leaves an oil which distils almost completely at 236—237° under 11 mm. pressure; the yellow oil thus obtained has a beautiful green fluorescence, does not dissolve in dilute caustic potash, and gives no coloration with ferric chloride.

0.2226 gave 0.5140 CO₂ and 0.1215 H₂O. C=62.97; H=6.06. 0.2360 , 0.5445 CO₂ , 0.1295 H₂O. C=62.92; H=6.09.
$$C_{19}H_{22}O_7$$
 requires C=62.98; H=6.07 per cent.

The constitution indicated above accords with the behaviour of the substance towards alcoholic ammonia, in which it dissolves, producing a red solution. This, after standing for 2 days, yields, on evaporation, a solid residue which is very soluble in alcohol, and crystallises from dilute alcohol in silky needles melting at 137°. The following analytical data, and the fact that the compound, on warming with alkali, evolves ammonia, indicate that it is the monamide derived from triethylic benzoyltrimethylenetricarboxylate.

0.2155 gave 0.4845 CO₂ and 0.1108 H_2O . C = 61.31; H = 5.71. 0.2795 ,, 10.5 c.c. nitrogen at 18° and 761 mm. N = 4.34. $C_{17}H_{19}NO_6$ requires C = 61.26; H = 5.70; N = 4.20 per cent.

Triethylic Acetyltrimethylenetricarboxylate,

$$\begin{array}{c} {\rm COOC_2H_5 \cdot CH} \\ {\rm COOC_2H_5 \cdot CH} \\ {\rm CO \cdot CH_3} \end{array}$$

Ethylic acetoacetate reacts with ethylic acetylenedicarboxylate and sodium ethoxide in a similar manner to the benzoylacetate, yielding a faintly yellow oil, the greater part of which distils at 186—187° under 13 mm. pressure.

0.2312 gave 0.4750 CO₂ and 0.1410 H₂O.
$$C = 56.03$$
; $H = 6.77$. $C_{14}H_{20}O_7$ requires $C = 56.0$; $H = 6.66$ per cent.

To the record of the work on the interaction of ketonic compounds VOL. LXXV.

and of ethylic malonate and its homologues with the ethylic salts of the acids of the acetylene series, we add the result of an experiment which is closely connected with the above research. It is based upon the following consideration. Since the substances with the -CiC-group readily form additive products under the influence of sodium ethoxide, it might be expected that a similar reaction would occur with compounds containing the NiC-group. Such a compound, which might be compared with the ethylic salts of acids of the acetylene series, would be ethylic cyanoformate, NiC-COOC₂H₅. This we prepared according to Weddige's method (J. pr. Chem., 1874, [ii], 10, 193) by distilling a mixture of ethylic oxamate and phosphoric anhydride, which we found to be much more convenient, and to give a better yield than that recommended by Wallach (Annalen, 1877, 184, 12).

Ethylic cyanoformate readily reacts with ethylic sodiomalonate suspended in absolute ether, but not in the manner we anticipated. The product, which smells strongly of hydrogen cyanide, gives, on acidifying with dilute sulphuric acid, an almost quantitative yield of triethylic methanetricarboxylate. A similar decomposition occurs on using ethylic salts of β -ketonic acids, such as ethylic acetoacetate or ethylic benzoylacetate. Ethylic cyanoformate therefore reacts in an analogous manner to ethylic chlorocarbonate.

In conclusion, the authors wish to express their thanks to the Government Grant Committee of the Royal Society for the funds kindly placed at their disposal for carrying out this and previous researches on ketonic compounds.

GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

LXXV.—Action of Hydrogen Peroxide on Carbohydrates in the Presence of Ferrous Salts.

By Robert Selby Morrell, M.A., Ph.D., and James Murray Crofts, B.A., B.Sc.

FENTON has shown, in the oxidation of tartaric acid by hydrogen peroxide in the presence of ferrous salts, that the CH·OH groups become oxidised to C·OH groups with the formation of dihydroxymaleic acid (Trans., 1894, 65, 899; 1895, 66, 774; 1896, 69, 546). Cross, Bevan, and Claude Smith (Trans., 1898, 73, 463) applied this method of oxidation to the carbohydrates glucose, lævulose, and cane sugar,

and found that substances were formed which reacted with phenylhydrazine at the ordinary temperature, and also reduced Fehling's solution in the cold. They were, however, unable to decide the nature of these substances, and, with their permission, we have examined the products of the reaction. In September, 1898, we communicated some of our results to the British Association, and showed that the first product belonged to the class of osones. We had not then isolated the osones, but their presence was recognised by the formation of phenylglucosazone when the solution of the oxidised glucose was treated with phenylhydrazine acetate at the ordinary temperature, and by the production of a methylphenylglucosazone by treatment of the oxidised glucose in the cold with methylphenylhydrazine. The formation of the latter is considered by Emil Fischer (Ber., 1889, 22, 87) to be one of the characteristic tests for the presence of glucosone. The solution of the glucosone reduced Fehling's solution strongly when slightly warmed, and formed precipitates with diamines, hydrazine hydrate, or benzoylhydrazine in the cold, and with aniline at a slightly higher temperature.

The action of hydrogen peroxide in the presence of ferrous iron is seldom such as to completely oxidise these sugars to osones; some of the carbohydrate is always left over, and if it is fermentable by yeast, it may be removed in that way from the glucosone which is not attacked by yeast. The osone freed from fermentable sugar can be isolated by dissolving it in absolute alcohol and precipitating with ether, and is as active towards organic bases as the glucosone described by Emil Fischer (loc. cit.).

The behaviour of levulose is almost identical with that of glucose under like conditions of treatment; glucosone is formed, and with this carbohydrate the action of hydrogen peroxide is more rapid than with glucose.

Arabinose, on oxidation, gives a substance resembling an osone, and the reaction is similar to that observed with the hexoses. The arabinosone obtained is identified by the formation both of phenylarabinosazone and of methylphenylarabinosazone at the ordinary temperature. Arabinose, however, even on warming with excess of methylphenylhydrazine, gives only the methylphenylhydrazone. Galactose, rhamnose, and even starch, under similar conditions of oxidation, give solutions which react with phenylhydrazine at the ordinary temperature, forming substances which are still under investigation. The results of the action of bromine water and of hydrogen cyanide on the oxidation products of glucose and lævulose will be communicated in a subsequent paper.

It would seem that the CH OH group contiguous to the aldehyde group in the carbohydrates is oxidised to CO, and that the aldehyde

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group in the presence of this oxidising agent is not affected. In the case of levulose, the primary alcohol group adjacent to the CO group undergoes oxidation to the CHO radicle, a transformation which Fenton (Trans., 1899,75, 1) has shown to occur with glycerol, mannitol, and sorbitol, yielding glycerose, mannose, and sorbose respectively.

EXPERIMENTAL.

Oxidation of Glucose by Hydrogen Peroxide.

A 10 per cent. aqueous solution of glucose containing 0.3 per cent. of crystallised ferrous sulphate is oxidised by hydrogen peroxide of 20 volume strength. The neutralised peroxide is added in quantities corresponding to 1/10 atom of oxygen per gram-molecule of glucose until an atomic proportion of oxygen has been allowed to act on a molecular proportion of glucose. At first, the action is slow, and several hours elapse before all the ferric iron formed is reduced to ferrous iron again. After the reaction with the first 1/10 atom of oxygen is over, a little lead acetate is added; the addition of hydrogen peroxide is then continued, care being taken that the ferric iron has passed back again to ferrous before more of the oxidising agent is employed. The rise in temperature during the oxidation is never great, being about 2-6°. When one atomic proportion of oxygen has been allowed to react, the solution is treated with basic lead acetate, avoiding an excess; the precipitate, which is never large in quantity, is filtered off, the lead completely removed by just sufficient sulphuric acid for precipitation, the filtrate neutralised by caustic soda, and the remaining glucose destroyed by fermentation for several days at 30° with well-washed brewers' yeast until a small quantity, on dilution and treatment with a fresh quantity of yeast, gives no further evolution of carbon dioxide. The dark solution, after filtration from the yeast, is treated with phenylhydrazine acetate at the ordinary temperature, and, after standing for half an hour, the orange precipitate is collected, washed with water, dilute alcohol, and ether, and dried in a vacuum. Thirty grams of glucose, under these conditions of oxidation, give 9 grams of osazone.

0.182, dried at 105°, gave 0.4027 CO_2 and 0.1021 H_2O . C = 60.3; H = 6.2. $C_{18}H_{22}N_4O_4$ requires C = 60.3. H = 6.1 per cent.

The osazone melts at 205° with decomposition, and is undoubtedly phenylglucosazone derived from glucosone, produced by the oxidation of glucose by hydrogen peroxide in the presence of iron.

Methylphenylglucosazone.—An aqueous solution of glucosone prepared as described above is warmed to 50° and treated with methylphenyl-

hydrazine dissolved in dilute acetic acid; an immediate turbidity ensues, and, on standing, a brownish-yellow precipitate separates. After being washed with water, dilute alcohol and ether, and recrystallised from benzene, methylphenylglucosazone forms slightly yellow, needle-shaped crystals, melting at 152° with decomposition, and giving the following numbers on analysis:

0·1505 gave 0·3413 CO_2 and 0·095 H_2O . C=61·85; H=6·95. 0·1095. , 13·6 c.c. of moist nitrogen at 23° and 766 mm. N=14·15. $C_{20}H_{26}N_4O_4$ requires C=62·1; H=6·7; N=14·5 per cent.

Separation of the Glucosone.—The aqueous solution of the glucosone is concentrated to a syrup at 50° in a vacuum, the syrup treated with absolute alcohol, filtered, the alcoholic solution concentrated in a vacuum at 50°, and the last traces of alcohol removed by dry ether. The residue, on treatment with absolute alcohol, dissolves, and after the addition of dry ether, a small quantity of a white, hygroscopic solid is obtained, which soon changes to a syrup, is hardly sweet to the taste, reduces Fehling's solution when slightly warmed, and reacts readily with phenylhydrazine at the ordinary temperature. 1.3 grams of the white solid gave a relatively large precipitate with phenylhydrazine in the cold, and, after warming slightly, the yield amounted to 0.5 gram of phenylglucosazone. A control experiment with 1.3 grams of glucose showed that no precipitate was formed with phenylhydrazine acetate at the ordinary temperature, and that 0.7 gram of osazone was obtained on warming for about a quarter of an hour. The identity of the phenylglucosazone from glucosone was proved by the melting point, 205°, and by a nitrogen determination.

0·1091 gave 14·8 c.c. of moist nitrogen at 23° and 761 mm. $N=15\cdot3$ $C_{18}H_{22}N_4O_4$ requires $N=15\cdot6$ per cent.

The aqueous solution of the glucosone gives precipitates with orthophenylenediamine or benzoylhydrazine at the ordinary temperature, and with aniline acetate on slightly warming. The oxime has not as yet been obtained crystalline.

Oxidation of Lavulose by Hydrogen Peroxide.

Under conditions similar to those described in the case of glucose, lævulose gives an osazone with phenylhydrazine acetate at the ordinary temperature, which after recrystallisation from dilute alcohol, melts at 205° and is phenylglucosazone.

0.1858 gave, after drying at 100°, 0.4085 CO₂ and 0.1050 H_2O . C = 59.96; H = 6.3.

 $C_{18}H_{22}N_4O_4$ requires C = 60.3; H = 6.1 per cent.

The oxidation product from 30 grams of lævulose yields 10.5 grams of the osazone after standing for \(\frac{3}{4} \) hour in the cold with phenylhydrazine. Lævulose seems to be more easily oxidised than glucose by hydrogen peroxide, as the reaction is completed easily in a day, whereas the addition of hydrogen peroxide has to be continued during two days in the case of the latter.

Oxidation of Galactose by Hydrogen Peroxide.

Galactose, when oxidised under like conditions with one atomic proportion of oxygen per gram-molecule of sugar, gives, with phenylhydrasine acetate, a red precipitate which is soluble in ether. As we could not recrystallise this satisfactorily, we used methylphenylhydrazine instead, and purified the oxidation product by concentration in a vacuum, treatment with absolute alcohol, subsequent concentration in a vacuum, and removal of the last traces of absolute alcohol by ether. The syrup so obtained contained galactose, as it yielded mucic acid (m. p. 213°) on oxidation with nitric acid, and with methylphenylhydrasine in the cold gave an immediate orange precipitate consisting of galactose methylphenylhydrazone readily soluble in hot water, and another substance insoluble in water but soluble in hot benzene. Galactose methylphenylhydrazone crystallises in colourless needles from hot water and melts at 187° with decomposition.

0.1725, dried at 100° , gave 0.3460 CO_{9} and $0.1102 \text{ H}_{2}\text{O}$. C = 55.25; H = 7.1.

0·1955, dried at 100°, gave $16\cdot2$ c.c. moist nitrogen at 18° and 773 mm. $N=9\cdot7$.

 $C_{13}H_{20}N_2O_5$ requires C = 54.93; H = 7.0; N = 9.8 per cent.

The substance insoluble in hot water is under investigation.

Oxidation of Arabinose by Hydrogen Peroxide.

A 5 per cent. aqueous solution of arabinose containing 0.5 per cent. of crystallised ferrous sulphate is oxidised by the careful addition of neutralised hydrogen peroxide of 20 volume strength in quantities corresponding with 1/10 atom of oxygen per gram-molecule of sugar, until one atomic proportion of oxygen has been added. The action is at first slow, but after half the requisite quantity of oxygen has been added there is a decided colour change on addition of the oxidising agent, the solution becoming greenish-blue; the colour, however, is only temporary, and disappears when the hydrogen peroxide has been used up. It is advisable to keep the solution cool, for there is often a decided rise of temperature during the addition of the oxidising

agent. When one atomic proportion of oxygen has been added, the solution is treated with normal and basic lead acetate, avoiding an excess of the latter, the solution filtered, and the lead in solution removed completely by just sufficient sulphuric acid for precipitation. The clear solution reacts readily with phenylhydrazine in the cold, giving an osazone which is easily soluble in alcohol or ether; the yield amounts to 17 per cent. of the weight of sugar taken, if the mixture is left for 2 hours at the ordinary temperature before filtration. After recrystallisation three or four times from dilute alcohol, the osazone melted at 158°, and on analysis gave the following numbers.

- 0·17, dried in a vacuum, gave 0·3885 CO_{q} and 0·0905 $H_{q}O$. C = 62·3; H = 5·8.
- 0·111, dried at 100°, gave 16 c.c. moist nitrogen at 19° and 770 mm. N = 16.75.
 - $C_{17}H_{20}O_3N_4$ requires C = 62.2; H = 5.5; N = 17.0 per cent.

The substance therefore is arabinosazone, derived from the osone obtained by the oxidation of arabinose with hydrogen peroxide.

Methylphenylarabinosazone.—A solution of the arabinosone reacts with methylphenylhydrazine at the ordinary temperature; it is advisable, however, to warm it to 40°, and then to add not quite the calculated quantity of methylphenylhydrazine acetate. When cold, the precipitate is collected, washed with water and ether, and dried in a vacuum; a brownish-yellow solid is thus obtained which, when recrystallised from benzene, gives yellowish, needle-shaped plates melting at 168—170° with decomposition. The yield of crude osazone is 25 per cent. of the weight of the arabinose taken.

- 0.175, dried in a vacuum, gave 0.4104 CO_3 and 0.1055 H_2O_4 . C = 63.9; H = 6.7.
- 0.173, dried at 105° until constant, gave $0.4024 \, \text{CO}_2$ and $0.106 \, \text{H}_2\text{O}$. C = 63.4; H = 6.8.
- 0.1258, dried at 105° , gave 17.2 c.c. moist nitrogen at 17° and 753 mm. N = 15.4.
 - $C_{19}H_{24}N_4O_3$ requires C = 64.0; H = 6.7; N = 15.7 per cent.

Arabinose with methylphenylhydrazine gives only the hydrazone even when warmed with an excess on the water-bath. An aqueous solution of 3 grams of arabinose, when warmed for a short time on the water-bath with 4.5 grams of methylphenylhydrazine dissolved in dilute acetic acid, gives a white, crystalline precipitate of the hydrazone, which, after recrystallisation from dilute alcohol, melts at 163°; it is only sparingly soluble in benzene.

- 0.1812, dried at 100° , gave 0.3784 CO_2 and 0.1213 H_2O . C=56.9; H=7.4.
- 0.1687, dried at 100°, gave 17.0 c.c. moist nitrogen at 15° and 753 mm. N = 11.5.
 - $C_{12}H_{18}N_2O_4$ requires C = 56.7; H = 7.1; N = 11.7 per cent.

The solution of arabinosone obtained by oxidation with hydrogen peroxide in the presence of ferrous sulphate reacts easily with aniline acetate, giving a dark brown, flocculent precipitate on warming on the water-bath; it reacts also easily with parabromophenylhydrazine in the cold, giving what is probably an osazone. Arabinose is perhaps more completely oxidised than glucose, and its disappearance can be noticed by the solution failing to give the colour reaction with phloroglucinol towards the end of the oxidation.

The ease with which methylphenylhydrazine gives easily crystallisable hydrazones when warmed with arabinose and galactose for ashort time on the water-bath, may be of use in the separation of these two sugars from glucose and lævulose, which, as Emil Fischer has shown, do not react with it. The sugar so separated might be regenerated from the hydrazone, as is the case with mannose.

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LXXVI.—The Action of Alkyl Haloids on Hydroxylamine.

Formation of Substituted Hydroxylamines and
Oxamines.

By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING, B.Sc.

In two previous papers (Proc., 1894, 10, 138; Trans., 1896, 69, 839), the authors have shown that methylic iodide readily reacts at the ordinary temperature with a solution of hydroxylamine in methylic alcohol, forming the hydriodide of a trimethylhydroxylamine and trihydroxylamine hydriodide, (NH₂OH)₂,HI, together with a dihydroxylamine hydriodide, (NH₂OH)₂,HI. These salts are separated by fractional crystallisation. A short description has been also given of the method of formation and properties of the free "trimethylhydroxylamine" and of its salts. Our account of this remarkable reaction has been confirmed by the experiments of Lobry de Bruyn (Rec. Trav. Chim., 1896, 15, 185).

In the present paper, the authors give a full account of their observations on this subject, and also of the action of other alkyl iodides on hydroxylamine.

Briefly summarised, the results prove that, by the action of methylic iodide on hydroxylamine, the salt of a stable trimethyl derivative is readily obtained, and a complete study has been made of the principal properties of the base and its salts. It is proved that this trimethylhydroxylamine must be represented by the formula $(CH_3)_3NO$, since it does not contain a methoxyl group. It will be convenient to designate this isomeride of a true trimethylhydroxylamine, $(CH_8)_2NOCH_3$, as trimethyloxyammonia or trimethyloxamins. No other substituted hydroxylamine could be isolated from the products of the action of methylic iodide on an alcoholic solution of hydroxylamine.

By the further action of methylic iodide on trimethyloxamine, the salt of a tetramethyloxyammonium has been obtained. The properties of this remarkable base, whose structure is represented by the formula $(CH_3)_3N(OCH_3)OH$, and three of its principal salts are described. Both the tri- and tetra-methyl derivatives decompose when heated in acid solution, furnishing in the case of the trimethyl compounds formaldehyde and dimethylamine, and in the case of the tetra-compound formaldehyde and trimethylamine.

By the reaction of ethylic iodide with hydroxylamine, the hydriodide of β -diethylhydroxylamine, and by the further action of the haloid, the hydriodide of triethyloxamine, have been obtained. There is no evidence of the production of a mono-substituted hydroxylamine under these conditions. The diethyl base is a liquid strongly alkaline in reaction and possessing powerful reducing properties; it is decomposed on heating, forming acetaldehyde and ethylamine. The properties of this compound show that it is a true hydroxylamine derivative, represented by the formula N(CoH5)cOH. The triethyloxyammonia, however, closely corresponds in its properties with the trimethyl and must therefore be represented as a triethylcompound. oxamine, (C₂H₅), NO. In an analogous manner, it breaks up on heating into acetaldehyde and diethylamine. It therefore appears that methylic iodide reacts with hydroxylamine to form at once the trimethyloxyammonia, whilst ethylic iodide forms first a diethyl hydroxylamine, and afterwards, not a triethylhydroxylamine, but the isomeric triethyloxyammonia, which, probably for stereochemical reasons, appears to be the stable configuration. By the reaction of normal propylic and secondary propylic iodides with hydroxylamines, dipropyl- and di-isopropyl-hydroxylamines have been prepared.

In conclusion, the authors discuss the recent work of Hantzsch and Hilland (Ber., 1898, 31, 2058) on the subject, and show ground for not accepting the conclusions of these authors,

Action of Methylic Iodide on Hydroxylamine; Formation of Trimethyloxyammonia, or Trimethyloxamine.

When methylic iodide is added to a solution of hydroxylamine in methylic alcohol (prepared by the interaction of the hydrochloride and sodium methoxide in molecular proportion), much heat is evolved, and on concentrating the solution a mixture of the hydriodides of trimethyloxyammonia and of hydroxylamine crystallises out. These compounds may be separated by solution in methylic alcohol and fractional precipitation with ether. The hydroxylamine hydriodides, $(NH_2OH)_2$, HI and $(NH_2OH)_3$, HI, and a little sodium chloride separate first, trimethyloxamine hydriodide collects in the later fractions, whilst some quantity of hydroxylamine, possibly in the form of the unstable normal hydriodide, remains dissolved.

A rather better yield of the trimethyloxyammonia salt is obtained if, after the first action has subsided, the mixed solutions are heated for a short time on the water-bath under a reflux condenser. After the liquid is cold, if ether is added, a considerable quantity of the hydriodide of trimethyloxamine is thrown out, the greater part of the hydroxylamine salts remaining in solution. The salt is purified by cautiously adding ether to its solution in methylic alcohol, or by crystallisation from warm water. The salt melts near 127° with decomposition, formaldehyde being evolved, and it is gradually decomposed at 100°.

By the reaction of the hydriodide with a solution of silver sulphate, trimethyloxamine sulphate is obtained as a crystalline, deliquescent mass very soluble in water and in alcohol. The crystals melt at 155—156° with decomposition. By the action of barium chloride on a solution of the sulphate, the hydrochloride is obtained in prismatic crystals melting with decomposition at 205—210°. This salt is also readily soluble in water and in hot methylic alcohol. When an aqueous solution of the sulphate is mixed with barium carbonate in the cold, a vigorous effervescence takes place, carbon dioxide being evolved, and the base liberated.

Analysis of the hydriodide gave the following results:

- I. 1.0166 gave 1.166 AgI. I = 61.98.
- II. 0.3482 ,, 0.3997 AgI. I = 62.04 N(CH₃)₃OHI requires I = 62.56 per cent.

The platinichloride forms well-defined rhombohedra, very soluble in water and methylic alcohol, less soluble in ethylic alcohol. It melts with decomposition at 228—229°.

Analysis of this salt gave the following result;

0.368 gave 0.129 Pt. Pt = 35 per cent. $[N(CH_3)_8O]_9$, H_2 PtCl₆ requires Pt = 34.8 per cent.

The aurichloride crystallises in yellow octahedra readily soluble in hot water; they melt near 200°.

Analysis gave the following result:

0.0978 gave 0.0464 Au. Au = 47.4 per cent. $(CH_3)_8NO_7HAuCl_4$ requires Au = 47.5 per cent.

The picrate melts at 196-198°.

Trimethyloxyammonia (Trimethyloxamine).

The free base is obtained from the sulphate by adding a slight excess of baryta water to its aqueous solution, carbon dioxide is passed through the liquid in order to remove the excess of baryta, and the filtrate is then evaporated nearly to dryness on the waterbath. On cooling, the liquid residue crystallises in radiating needles which melt at 96°, and are not volatile. The base is very deliquescent, and is soluble in water and methylic alcohol, less soluble in ethylic alcohol, and insoluble in ether; from the solution in hot ethylic alcohol, it crystallises in long needles. The aqueous solution has a powerfully alkaline reaction to litmus and methyl-orange, although not to phenolphthalein, and a slightly soapy taste and smell. The aqueous solution does not reduce Fehling's solution. When added to a solution of silver nitrate, a white precipitate is produced which turns black on warming. It has no effect on either a neutral or an acid solution of potassium iodide. A solution of ferrous sulphate quickly reduces a solution of the base, with separation of ferric hydroxide.

By analysis, it was ascertained that this crystalline compound is a dihydrate of trimethyloxamine. A determination of the nitrogen by combustion with soda lime gave the following results:

- I. Specimen recrystallised from alcohol by addition of ether. II. Specimen crystallised from water.
 - I. 0.1223 gave 0.0152 nitrogen. N = 12.4.
 - II. 0.1338 ,, 0.0167 ,, N = 12.5. (CH₂)₈NO,2H₂O requires N = 12.6 per cent.

Determination of the carbon and hydrogen in two specimens recrystallised from alcohol furnished the following data:

0.1848 gave 0.1920 H_2O and 0.2240 CO_2 . C=33; H=11.5. 0.188 ,, 0.1952 H_2O ,, 0.2263 CO_2 . C=32.8; H=11.6. $(CH_3)_3NO_2H_2O$ requires H=11.7. C=32.4 per cent.

It therefore appears that this hydrate does not lose water by

recrystallisation from a mixture of alcohol and ether; heated above 110°, however, water is expelled, and near 180° the base suffers complete decomposition, formaldehyde and trimethylamine being among the products. So far, we have not succeeded in obtaining the anhydrous base. As is shown later, there is no foundation for the recent statement of Hantzsch and Hilland (loc. cit.) that this compound, first described by us in 1894, is really a carbonate of the base.

Trimethyloxamine forms salts by direct combination with acids; these salts exhibit an acid reaction in aqueous solution.

On the addition of mercuric chloride to an aqueous solution of the base, a double compound crystallises out.

0.2606 gave 0.2181 AgCl. Cl = 20.7. $(CH_8)_3NO, HgCl_2$ requires Cl = 20.5 per cent.

The aqueous solution of the base throws down, from a solution of copper sulphate, a pale blue precipitate which is insoluble in water and alcohol, and appears to be a basic double sulphate. The hydrate of trimethyloxamine is a very stable substance; when boiled with a solution of caustic potash, it is only slowly decomposed; if heated with hydrochloric acid in a sealed tube at 100°, very little change is produced. When heated with sulphuric acid (33 per cent.) in a sealed tube at 110°, formaldehyde and dimethylamine were produced, the latter being identified by means of its platinichloride, which, on analysis, furnished the following result:

0.0597 gave 0.0234 Pt. Pt = 39.2. $[NH(CH_8)_9]_{9}H_2PtCl_6$ requires Pt = 39.0 per cent.

This decomposition of trimethyloxamine may therefore be represented by the following equation: $(CH_3)_3NO = CH_2O + NH(CH_3)_2$.

When the substance is heated either with hydriodic acid or with a mixture of tin and hydrochloric acid, dimethylamine is formed. But since no methylic iodide is produced by the action of hydriodic acid, proving the absence of a methoxyl-group, it was suspected that the decomposition represented above had occurred previous to reduction. An experiment was therefore made, in which an aqueous solution of the base was left for several days in contact with zinc dust; the liquid was then distilled into hydrochloric acid, and the platinichloride prepared and analysed.

0.865 gave 0.0321 Pt. Pt = 37.1. 0.582 gave 0.214 Pt. Pt = 36.8. $[N(CH_8)_8]_2, H_2PtCl_6$ requires Pt = 37.0 per cent.

Reduction with a mixture of zinc and dilute hydrochloric acid furnished the same product.

The reduction of trimethyloxamine may therefore be represented by the equation; $N(CH_3)_3O + H_2 = H_2O + N(CH_3)_3$.

We consider that these experiments conclusively prove the constitution of this base. The fact that formaldehyde and dimethylamine are produced on heating its salts seemed at first to be strong evidence in favour of the existence of a methoxyl group, and therefore of the formula $(CH_3)_2NOCH_3$. This, however, is negatived by the non-production of methylic iodide, by the action of hydriodic acid, and by the formation of trimethylamine on reduction with zinc dust. Moreover, according to the observations of Kjellin (Ber., 1893, 26, 2377), β -methylhydroxylamine, $NH(CH_3)OH$, is decomposed, when heated with hydrochloric acid in a sealed tube at 200°, into formaldehyde and ammonia, whilst the β -ethyl compound is similarly decomposed. In like manner, Walder (Ber., 1886, 19, 1629) has shown that β -dibenzylhydroxylamine, $(C_7H_7)_2NOH$, furnishes benzaldehyde and benzylamine.

Action of Methylic Iodide on Trimethyloxamine; Formation of Trimethylmethoxyammonium Iodide.

When an alcoholic solution of trimethyloxamine is heated with an excess of methylic iodide, formaldehyde is formed and crystals separate out which on analysis proved to be tetramethylammonium iodide. After recrystallisation from water, the salt exhibited all the properties of this substance, and on analysis gave the following data:

0.1853 gave 0.2153 AgI. I = 62.8.

 $N(CH_3)_4I$ requires I = 63.2 per cent.

The platinichloride was prepared and analysed.

0.0837 gave 0.0295 Pt. Pt = 35.2.

 $[N(CH_8)_4Cl]_{2}$, $PtCl_4$ requires $Pt = 35 \cdot 1$ per cent.

On the addition of ether to the liquid from which the tetramethylammonium salt had been separated, the substance crystallises out in plates, which have been proved to be tetramethyloxyammonium iodide, $(CH_s)_8NOCH_g$, I.

Further experiments have shown that if, instead of heating the mixture, the reaction is allowed to take place at the ordinary temperature, the formation of the tetramethylammonium iodide is almost entirely avoided. The following method has been found to be most satisfactory. Two grams of trimethyloxamine are dissolved in about 5 c.c. of methylic alcohol, 4 grams of methylic iodide added, and the mixture is left in a closed vessel for about 24 hours. The crystals which separate are removed and recrystallised from warm methylic alcohol, washed with ethylic alcohol, and dried on a porous tile in a desiccator. By the addition of ether to the mother liquor, more

crystals may be obtained and recrystallised and dried as described. Analyses of a number of a number of specimens were made, with the following results:

```
0.2282 gave 0.2488 silver iodide.
                                Indine =58.9 per cent.
0.2434
           0.2656
                                       = 58.9
        ,,
                                                  ,,
0.4995
                                       = 57.9
           0.5855
        **
                          "
                                                  ,,
0.5247
        ., 0.5734
                                       = 59.0
0.1630
        . 0.1749
                                       =58.0
0.3819
        ., 0.4117
                                       =58.3
            N(CH_a)OI requires I = 58.5 per cent.
```

The amount of nitrogen in the salt was determined by combustion with soda lime, the percentage of nitrogen found = 66.9. Calculated for $N(CH_8)_4OI$, N=6.45 per cent.

The iodide of the tetra-base crystallises in white plates. When heated, formaldehyde is evolved. It is soluble in water and in hot methylic alcohol, but nearly insoluble in cold ethylic alcohol and in ether. It is decomposed by a solution of caustic potash into methylic alcohol and trimethyloxamine in accordance with the following equation: $N(CH_8)_8OCH_8I + NaOH = N(CH_8)_8O + CH_8OH + NaI$.

When an aqueous solution of the salt is heated for an hour and a half at 150° in a closed tube, formaldehyde is split off, and trimethylamine formed. This was identified by the analysis of its platinic bloride.

 $0.0605 \text{ gave} \cdot 0.0223 \text{ Pt.} \quad \text{Pt} = 36.9.$

$$[N(CH_8)_8]_2$$
, H_2 PtCl₆ requires Pt = 37.0 per cent.

When heated with hydriodic acid, the iodide is decomposed, with formation of methylic iodide and dimethylamine. The base was recognised by the analysis of the platinichloride:

0.0445 gave 0.0173 Pt. Pt = 38.9.

 $[NH(CH_8)_2]_9$, H_9PtCl_6 requires Pt = 39.0 per cent.

In this reaction, formaldehyde is also produced

$$N(CH_3)_3OCH_3I + HI = NH(CH_3)_2HI + CH_2O + CH_3I.$$

It is therefore clear that the compound contains one methoxyl group.

In this decomposition, the methoxyl group is evidently first split off, and then the trimethyloxamine decomposed in the manner described in a previous section of this paper.

When reduced by standing with zinc dust in aqueous solution, the hydriodide is converted into trimethylamine,

$$N(CH_8)_8OCH_8I + H = CH_8OH + N(CH_8)_8HI.$$

The crystalline platinichloride of the amine was prepared and analysed.

0.0632 gave 0.0236 Pt. Pt = 37.3. $[N(CH_8)_8]_9$, H_9 PtCl₈ requires Pt = 37.0 per cent.

Trimethylmethoxyammonium chloride was prepared by decomposing an aqueous solution of the iodide with silver sulphate, filtering, and decomposing the sulphate by means of barium chloride. The filtered liquid, when evaporated, left a hygroscopic residue of the chloride which crystallised in needles. It readily formed a platinichloride, crystallising in orange-red, feathery needles, which, on analysis, furnished the following result:

0.0644 gave 0.0213 Pt. Pt = 33.1. $[N(CH_s)_4OCl]_{2r}$ PtCl₄ requires Pt = 33.1 per cent.

The aurichloride is almost insoluble in cold water and alcohol. A well crystallised specimen was analysed:

0.1833 gave 0.0848 Au. Au = 46.3. $N(CH_3)_4OCl_4AuCl_3$ requires Au = 46 per cent.

Trimethylmethoxyammonium Hydroxide, (CH₃)₃N(OCH₃)OH.

The free base has so far been obtained only in aqueous solution by decomposing a solution of the iodide first with silver sulphate and then decomposing the sulphate thus formed with baryta. The filtrate was alkaline to litmus paper. That it contained the free base was proved by neutralising with hydrochloric acid, and converting the chloride into the platinichloride, which was analysed. In order to isolate the base, the alkaline solution was distilled, when a strongly alkaline substance collected in the early fractions; so far, however, we have not been able to prepare the substance in a pure state. The properties of the aqueous solution show that it is a strongly basic substance. Further attempts will be made to isolate it in a state of purity.

Action of Benzylic Chloride on Trimethyloxamine.

We find that benzylic chloride reacts with trimethyloxamine, forming benzaldehyde and trimethylamine, which by further reaction passes into benzyltrimethylammonium chloride. It may therefore be concluded that in the action of methylic iodide on trimethyloxamine, the formaldehyde is derived from the oxidation of the methoxyl group of the tetra-derivative which is first formed, but subsequently in great part decomposed.

Action of Ethylic Iodide on Hydroxylamine; Formation of β-Diethylhydroxylamine.

Unlike the case of methylic iodide, when ethylic iodide is added in excess to a solution containing about 10 per cent. of hydroxylamine in methylic alcohol, little or no heat is evolved. After standing in a stoppered bottle for a day, crystals separate, which prove to be trihydroxylamine hydriodide, (NH₂OH)₃HI. The mother liquor is concentrated to a small volume by distilling it under reduced pressure on the water-bath, by which means the liberation of iodine is avoided. On cooling, a further quantity of crystals, chiefly composed of the same hydriodide, separate out. The residual liquid does not now furnish any crystals either by further concentration or by the addition of ether or other liquids. After several trials, the following process was adopted for the isolation of the other products of the reaction.

The very concentrated solution is diluted with water, and a strong solution of sodium carbonate added in slight excess, the liquid is then repeatedly extracted with ether (free from acetone) and the ethereal solution dried by means of calcium chloride. By careful distillation of the ethereal solution, the whole of the ether may be separated, leaving an oily liquid which, when distilled, mostly comes over between 130° and 134°.

The substance thus obtained is a highly refractive, volatile liquid having a distinctive, rather fragrant odour. Its specific gravity is 0.8771 at 15°/15°; it is soluble in water, and mixes with alcohol and ether in all proportions, the aqueous solution being strongly alkaline to litmus. When the solution is added to cupric sulphate, a pale blue precipitate insoluble in excess is thrown down; on very gently warming or on standing, this precipitate suffers reduction, forming cuprous oxide, whilst, on the addition of potash solution to the precipitate, cuprous oxide is immediately produced. When added to a solution of silver nitrate, a white precipitate is formed which at once turns black and quickly becomes metallic silver, forming a mirror on the tube even in the cold. Mercuric chloride is reduced at first to calomel and afterwards to metallic mercury. Acetyl chloride acts energetically on the substance, forming a very hygroscopic hydrochloride crystallising in needles, which is the salt of an acetyl derivative.

Of the salts of this base, the oxalate crystallises most readily. It is obtained by adding an ethereal solution of anhydrous oxalic acid to an ethereal solution of the base; the salt crystallises out in plates which are recrystallised by the addition of ether to a solution in methylic alcohol. The prismatic crystals melt at 136—137°.

On precipitation with calcium acetate,

0.7398 gave 0.1560 CaO. $H_2C_2O_4 = 33.65$. $[N(C_2H_5)_2OH]_9, H_2C_2O_4$ requires $H_2C_2O_4 = 33.58$ per cent.

When a solution of the base is neutralised with hydrochloric acid, and the liquid evaporated to dryness on the water-bath, a gummy, hygroscopic residue is obtained which cannot be crystallised. The platinichloride could not be obtained, owing to the powerful reducing action of the substance, platinum being invariably precipitated. Metallic gold is at once produced when a solution is added to the aqueous auric chloride.

When an aqueous solution of the base, slightly acidified with acetic acid, is heated in a sealed tube to 170—180° for 2 hours, the whole of the compound is decomposed, the liquid containing the condensation products of acetaldehyde, and when made alkaline and distilled into dilute hydrochloric acid, the hydrochloride of a base is obtained which exhibits all the properties of ethylamine hydrochloride. It crystallised in needles, was deliquescent, and melted on the water-bath. The platinichloride was prepared and analysed.

0.0452 gave 0.0176 Pt. Pt = 38.9. $(NH_2C_2H_5)_{2}$, H_2 PtCl₆ requires Pt = 39.0 per cent.

When the oxalate is heated for about an hour with boiling hydriodic acid, no ethylic iodide is formed. The base distilled from the residue exhibited all the properties of diethylamine. The platinichloride was prepared and analysed.

0.1052 gave 0.0367 Pt. Pt = 34.9. $[NH(C_2H_5)_2]_2, H_2PtCl_6 \text{ requires } Pt = 35.1 \text{ per cent.}$

There is therefore no doubt that the principal product of the action of ethylic iodide on hydroxylamine is a true β -diethylhydroxylamine, $(C_2H_5)_2N\cdot OH$.

Ethylic chloride reacts with hydroxylamine less readily, forming the same hydroxylamine which also results from the action of ethylic iodide in the presence of sodium ethoxide.

A diethylhydroxylamine having nearly the same boiling point was prepared by Kissel (J. Russ. Chem. Soc., 1887, 109—113) by the action of zinc ethyl on nitroethane; it may be that this substance is identical with that now described, although Kissel appears to have taken a different view of its constitution.

The β-diethylhydroxylamine now isolated is isomeric, not identical with either of the two diethylhydroxylamines described by Lossen (Annalen Suppl., 1868, 6, 238; Annalen, 1889, 252, 230), one of which is undoubtedly an ethoxyl derivative; the constitution of the other appears to be doubtful.

Action of Ethylic Iodide on Disthylhydroxylamine; Formation of Triethyloxamine (Triethyloxyammonia).

When an excess of ethylic iodide is added to an ethereal solution of the diethyl base, a thick, sticky liquid gradually separates; this substance proves to be the hydriodide of a triethyl compound. It is freely soluble in water and alcohol, but insoluble in ether. It is gradually decomposed at 100°, iodine being liberated; so far it has not been possible to crystallise this salt; the base was separated by exactly the same process which has been described in connection with the trimethyl base.

It is a colourless, crystalline, very deliquescent solid. Its aqueous solution has a somewhat soapy smell and is strongly alkaline, but does not reduce Fehling's solution. When added to aqueous cupric sulphate, a pale blue precipitate is thrown down. With silver nitrate, it furnishes a white precipitate which blackens when warmed.

The hydrochloride was obtained by adding barium carbonate to a solution of the sulphate, the latter having been produced from the hydriodide by the action of silver sulphate; it crystallises in deliquescent needles, soluble in alcohol and in water. The platinichloride is best prepared by mixing alcoholic solutions of the hydrochloride and platinic chloride, and then gradually adding ether, when the double salt crystallises out. It is very soluble in water, less soluble in methylic alcohol, and still less in ethylic alcohol. It is best recrystallised from a mixture of equal proportions of the two alcohols by the addition of ether. On analysis, the platinichloride gave the following results:

0.0813 gave 0.0248 Pt. Pt = 30.5. $[(C_2H_5)_8NO]_2, H_2PtCl_6$ requires Pt = 30.3 per cent.

The aurichloride, $(C_2H_5)_8NO, HAuCl_{\nu}$ separates as an oil, which has not been crystallised.

The sulphate of this base crystallises in rosettes which are very deliquescent, and, like the other salts, it decomposes when heated, and even becomes coloured when kept at the ordinary temperature.

The picrate is precipitated when aqueous solutions of picric acid and the base are mixed. It crystallises in needles melting near 164°.

When a solution of the triethyloxamine sulphate is heated in a closed tube at 200°, condensation products of acetaldehyde are formed in the liquid, and a base is obtained the hydrochloride (m. p. 221°) of which is soluble in alcohol and in chloroform. By the analysis of the platinichloride, it was proved to be diethylamine.

0.0798 gave 0.0279 Pt. Pt = 35. $[(C_2H_5)_2NH]_3, H_2PtCl_6$ requires Pt = 35·1 per cent, When an aqueous solution of the triethyl base is allowed to stand for some days with zinc dust, the solution acquires an ammoniacal odour. On distilling the reduction product into dilute hydrochloric acid, the crystalline hydrochloride of triethylamine is obtained, and from this the very soluble platinichloride was prepared and analysed.

0.0518 gave 0.0165 Pt. Pt = 31.9.

 $[N(C_2H_5)_3]_{2}H_2PtCl_6$ requires Pt = 31.9 per cent.

Triethylamine was also formed by heating the base with concentrated hydriodic acid, but no ethylic iodide was formed.

From the properties and reactions described above, there can be no doubt that the substance is a triethyloxamine, corresponding very closely in its properties with the trimethyloxamine already noticed. It is a remarkable point of difference between the action of the two alkyl iodides upon hydroxylamine that the methylic compound acts very energetically at the ordinary temperature, evolving much heat and producing at once the trimethyloxamine; on the other hand, the action of ethylic iodide is much slower and less energetic, and virtually terminates with the production of diethylhydroxylamine, the triethyloxamine being only obtained in quantity by the action of ethylic iodide upon this base. It is also interesting to notice the great instability of the trialkylhydroxylamines, $N(CH_3)_2OCH_3$, $N(C_3H_5)_2OC_3H_5$. Neither by the action of methylic nor of ethylic iodide have these substances been isolated; they appear to change immediately into the isomeric tri-alkyloxamines, $(CH_3)_3N:O$, $(C_2H_5)_8N:O$.

A triethylhydroxylamine represented by the formula $(C_2H_5)_8NO$ has been obtained by Bewad (J. Russ. Chem. Soc., 1888, 20, 125) by the action of zinc ethyl on nitroethane. The authors have repeated this experiment, and have obtained a fair quantity of this base, which differs markedly from the triethyloxyammonia now described.

Action of Normal Propylic Iodide on Hydroxylamine; Formation of β-Dipropylhydroxylamine.

When a solution of hydroxylamine in methylic alcohol is mixed with normal propylic iodide and allowed to stand, very little action occurs even after 24 hours. On heating the mixture on the waterbath for about 3 hours, and then concentrating the solution, the hydriodides of hydroxylamine crystallise out; the residual liquid, which furnishes no more crystals when concentrated, is dissolved in water, made alkaline with sodium carbonate, and the liquid extracted with ether. The ethereal solution of the base is now dried with calcium chloride, filtered, and mixed with an ethereal solution of anhydrous oxalic acid. The white, crystalline precipitate of the

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oxalate was removed, and the salt recrystallised, first from hot ethylic alcohol, and afterwards by precipitating a solution in methylic alcohol with ether. It crystallises in rosettes melting at 139°. It is fairly soluble in water and methylic alcohol, slightly soluble in cold, but readily in hot, ethylic alcohol. The aqueous solution is strongly acid to litmus paper. By analysis, the salt is proved to be an acid oxalate of dipropylhydroxylamine.

0.3968 gave 0.1071 CaO. $H_2C_2O_4 = 43.4$. $(C_2H_7)_2NOH, H_2C_2O_4$ requires $H_2C_2O_4 = 43.5$ per cent.

The properties of the base, purified by means of the acid oxalate, have been carefully studied; it boils between 153° and 156° with very little decomposition; it is a colourless, mobile liquid, having a curious peppermint-like odour; it is readily soluble in alcohol and ether, less soluble in water. The aqueous solution is strongly alkaline, acts as a powerful reducing agent, and behaves with solutions of cupric sulphate, silver nitrate, and mercuric chloride in precisely the same manner as diethylhydroxylamine. Acetyl chloride reacts with the base, forming a crystalline acetyl derivative.

When reduced with zinc dust and acetic acid, the base is converted into dipropylamine, which was separated by distilling with an alkali into dilute hydrochloric acid. Dipropylamine hydrochloride forms prismatic crystals readily soluble in alcohol and chloroform; the platinichloride is soluble in water and alcohol, and crystallises from a mixture of alcohol and ether in prisms melting at 193—195°.

0.0679 gave 0.0217 Pt. Pt = 32. $[NH(C_3H_7)_2]_{27}H_2PtCl_6$ requires Pt = 31.9 per cent.

It is therefore proved that propylic iodide reacts with hydroxylamine, forming a true dipropylhydroxylamine, N(C₈H₇)₂OH, and, in this respect, its action resembles that of ethylic iodide.

Action of Isopropylic Iodids on Hydroxylamins; Formation of β -Di-isopropylhydroxylamins.

A solution of hydroxylamine in methylic alcohol was mixed with about a calculated quantity of isopropylic iodide and heated on the water-bath for about 12 hours, when the action seemed to be at an end. The solution when evaporated furnished a considerable quantity of crystalline hydriodides of hydroxylamine, which were removed, and the residual liquid concentrated until its consistence was almost syrupy; it was then mixed with water, sodium carbonate added, and the base extracted by repeated shaking with ether; the ethereal solution, having been dried with calcium chloride, was carefully distilled

and the residue left after the distillation of the ether was gradually heated in a paraffin bath, when a colourless, mobile liquid distilled between 137° and 142°, slight decomposition taking place. This liquid was then redistilled near the same temperature.

The liquid base thus prepared has a curious smell closely resembling that of Bewad's triethylhydroxylamine. Its general properties agree very closely with the diethyl- and dipropyl-hydroxylamines. It is soluble in water and miscible in all proportions with alcohol and ether; the aqueous solution is strongly alkaline to litmus, and fumes in contact with hydrochloric acid. It reacts with solutions of copper sulphate, silver nitrate, and mercuric chloride in exactly the same manner as the diethyl and dipropyl bases already described. salts appear to be extremely difficult, if not impossible, to crystallise. When ethereal solutions of oxalic acid and the base are mixed, no precipitate is formed, but on evaporation the oxalate is deposited as a sticky liquid. When dry hydrogen chloride is passed into the ethereal solution of the base, the sticky liquid collects in the bottom of the vessel. So far all attempts to obtain crystalline salts have failed. In order to ascertain the reduction products of this compound, a solution of the syrupy oxalate was warmed with a mixture of zinc dust and acetic acid; after the addition of alkali, the mixture was distilled into dilute hydrochloric acid, and this solution on evaporation left the hydrochloride entirely soluble in chloroform and alcohol. latter solvent, it crystallised in long, silky needles and showed all the properties of the hydrochloride of di-isopropylamine. The platinichloride dissolves readily in water and in alcohol. On adding ether to an alcoholic solution, it crystallises in orange-red tablets melting at 190-193°. On analysis, this salt was found to contain 31.9 per cent. of platinum, which is that required by the formula of dipropylamine platinichloride, [NH(C₃H₇)₂]₂, H₂PtCl₆.

These results prove that the compound obtained by the action of isopropylic iodide on hydroxylamine is the iodide of the true β -di-isopropylhydroxylamine, $(C_8H_7)_2NOH$.

An account of the action of methylic iodide on hydroxylamine has been recently given by Hantzsch and Hilland (Ber., 1898, 31, 2058). The authors are apparently unacquainted with our paper on the subject (Proc., 1894, 10, 138) which contains an account of the properties of the trimethyl derivative and its salts. We are unable to confirm their account of the properties of the trimethyloxamine hydriodide, which, contrary to their experience, we find to be, when pure, a perfectly stable salt, which does not gradually decompose with the separation of iodine. Neither can we confirm the statement that this salt, when dried in the desiccator, contains $\frac{1}{2}H_2O$. Contrary to their statement

that the sulphate cannot be obtained in a solid state, we find that it crystallises readily when an aqueous solution is evaporated on the water-bath. Hantzsch and Hilland assert that the crystalline base described by us in our former, and also in our present, paper is really the carbonate. We are quite unable to confirm the results of their experiments on this point, and many of their statements seem to us We have repeated our experiments with this base to be inconsistent. since their paper appeared, and we are satisfied with the correctness of our former conclusion, that the crystalline material is a hydrated base The analytical data recorded in the present and not a carbonate. paper are sufficient to prove that this is the case, although other facts may be mentioned which quite negative their conclusion. The aqueous solution does not effervesce with acids, neither does it give any precipitate with baryta water: moreover, the same crystalline substance may be obtained by carefully decomposing the hydriodide with silver hydroxide and evaporating the solution. The properties of the base itself, which Hantzsch and Hilland only obtained in aqueous solution, do not at all agree with our observations. We do not find that its aqueous solution is an energetic reducing agent, neither can we confirm the statement that it rapidly absorbs carbon dioxide from the air or distils with steam. We believe that the reducing action is a consequence of the impurity of the substance, which was probably contaminated with hydroxylamine. We are unable to confirm the statement that the base reduces Fehling's solution, or that it liberates iodine from potassium iodide; neither do we find that, on the addition of an alkali to the aqueous solution, trimethylamine is produced. are therefore obliged to reject the theoretical conclusion of Hantzsch and Hilland that trimethyloxyammonium hydrate is stable only in an entirely ionised state, in the form of its ions N(CH_a), and OH, and that in proportion as it is converted into the non-ionised state, NH(CH₃)₃(OH), as, for example, by the hydroxyl ions of the alkalis, it is decomposed into trimethylamine and hydrogen peroxide.

From a careful study of the properties of the pure base, we conclude that there is no evidence to show that the oxygen atom is in the "active" condition analogous to that of the oxygen atom in hydrogen peroxide and in this respect therefore differs from the alkylpiperidine oxides described by Wernick and Wolffenstein (Ber., 1898, 31, 1553). The oxamines now described correspond precisely in their general properties with those of the dimethylaniline oxide prepared by Bamberger and Tschirner by the action of hydrogen peroxide on dimethyaniline (Ber., 1899, 32, 3421). It will be seen, therefore, that we entirely question the accuracy of Hantzsch and Hilland's observations on the properties of the trimethyl derivative of hydroxylamine described by us in 1894.

The same authors have examined the action of ethylic iodide on hydroxylamine; they conclude from their experiments that, even in the presence of excess of ethylic iodide, the monethyl derivative is formed. This is quite contrary to our experience, for we have never been able to detect the formation of any mono- β -ethylhydroxylamine in the product of this reaction, which, as we show in the present paper, results in the formation of β -diethylhydroxylamine.

Hantzsch and Hilland's conclusion appears to be based on a single analysis of the hydriodide, which they state crystallises from the alcoholic solution after the hydroxylamine hydriodides have separated. It does not appear that the salt was even recrystallised before analysis. We are convinced that the method used for the separation of the supposed ethylhydroxylamine would be quite insufficient for the separation of a pure hydriodide of a substituted hydroxylamine from the accompanying hydroxylamine salts. We have indeed repeated the experiment in exactly the manner described in their paper; the crystalline substance thus obtained, proved not to be a substituted hydroxylamine at all, but apparently a compound of hydroxylamine and ammonium iodides. In order to identify the supposed β -ethylhydroxylamine, Hantzsch and Hilland caused it to react with paranitrobenzaldehyde, when they state that the N-ethyl-ether of paranitrobenzaldoxime is obtained melting at 123°. We have repeated this experiment with the product prepared by their method, but have obtained only paranitrobenzaldoxime, melting at 127°, which had no doubt been produced by reaction with the hydroxylamine contained in the supposed monethylhydroxylamine. The account given by Hantzsch and Hilland of the properties of the base and of its salts is very meagre and highly suggestive of an impure material.

Lachman (Ber., 1899, 32, 27) has recently pointed out, in opposition to the criticism of Hantzsch and Hilland, that he has obtained the triethylhydroxylamine by the method described by Bewad, in which zinc ethyl reacts with nitroethane, and that it has the properties attributed to it by him. This also is the experience of the present writers, who have pointed out above that Bewad's derivative is isomeric, and not identical, with the triethylhydroxylamine described in the present communication.

The authors have found that the substituted hydroxylamines and oxamines now described may be prepared by the direct action of hydrogen peroxide on the corresponding amines. An account of their results will be given in another paper.

Scientific Department, Imperial Institute, London, S.W. LXXVII.—The Condensation of Ethylic Acetonedicarboxylate and Constitution of Triethylic Orcinoltricarboxylate.

By DAVID SMILES JERDAN.

Shortly after its discovery, Cornelius and von Pechmann (Ber., 1886, 19, 1446) found that ethylic acetonedicarboxylate reacts easily with sodium, yielding the sodium derivative of a solid substance, $C_{16}H_{20}O_8$, which they showed to be a triethylic orcinoltricarboxylate. They pointed out that the condensation probably takes place in the following stages:—

(I) Ethylic acetonedicarboxylate reacts with its sodium derivative thus:—

(II) The formation of a cyclic compound then follows, owing to the removal of the elements of water. As is indicated by the dotted lines in the formula, this may take place in two ways, thus leading to two possible formulæ for the product, which, owing to a simultaneous molecular change, is a true benzene derivative:—

The immediate product of the condensation is, of course, a sodium derivative of triethylic orcinoltricarboxylate, alcohol vapour being evolved in the reaction.

Two years ago, a second condensation product was obtained by the author (Trans., 1897, 71, 1106) by the action of sodium on ethylic acetonedicarboxylate in benzene solution. The new substance was shown to be a lactone possessing the composition $C_{12}H_{10}O_7$, and to be a derivative of phloroglucinol.

More recently, von Pechmann and Wolman (Ber., 1898, 31, 2014) have found that triethylic orcinoltricarboxylate may also be prepared by dissolving ethylic acetonedicarboxylate in alcohol, saturating the

solution with hydrogen chloride and allowing the whole to stand for some weeks. After separation of the alcohol and hydrogen chloride in the usual way, the oily product is distilled in a vacuum. The distillation is stopped after a quantity of unchanged ethylic acetone-dicarboxylate has passed over, and the residue solidifies, when cold, to a crystalline mass of triethylic orcinoltricarboxylate. In the same paper, the authors point out that when ethylic acetonedicarboxylate, to which some alcohol has been added, is treated with sodium, the lactone $C_{19}H_{10}O_7$ is formed.

The following paper falls naturally into two parts. The first of these deals with new methods of formation of the two condensation products already known, and contains a discussion of the nature of the reactions involved in the formation of triethylic orcinoltricarboxylate; the preparation and properties of a new condensation product which has been shown to be a diethylic hydrogen orcinoltricarboxylate are also described. The second part of the paper contains the results of an investigation into the constitution of triethylic orcinoltricarboxylate.

I. CONDENSATION OF ETHYLIC ACETONEDICARBOXYLATE.

Formation of Triethylic Orcinoltricarboxylate and of the Lactone $C_{12}H_{10}O_7$.

The author was led to investigate more closely the action of various condensing agents on ethylic acetonedicarboxylate,* by observing that in the preparation of its ethyl substitution products by the action of ethylic bromide on the sodium derivatives of the ester, a small amount of triethylic orcinoltricarboxylate † is formed. Since it seemed pro-

* The preparation of acetonedicarboxylic acid by the action of fuming sulphuric acid on anhydrous citric acid (von Pechmann, Annalen, 1891, 261, 157) may with advantage be shortened by omitting the tedious process of drying the citric acid and powdering the pasty product obtained. The fuming sulphuric acid used must contain an extra amount of sulphuric anhydride sufficient to combine with the water of crystallisation of the citric acid. The following process has given excellent results. Five hundred grams of powdered commercial citric acid are heated with 1000 grams of fuming sulphuric acid (15 per cent. SO₃) in the manner described by von Pechmann, and after the action is over 500 grams of finely crushed ice are added. The acetonedicarboxylic acid which separates may be conveniently collected on a large Buchner's funnel lined with stout flannel, pressed firmly down to remove as much sulphuric acid as possible, and finally dried by means of porous plates.

The crude ethylic ester, obtained by mixing the acid with alcohol and saturating with hydrogen chloride, always contains ethylic acetoacetate, which is present in greater amount when the crude acetonedicarboxylic acid has been insufficiently separated from adhering sulphuric acid. At the best, the crude ethylic salt contains about 80 per cent. of ethylic acetonedicarboxylate.

† Rimini (Gazzetta, 1896, 26, ii, 325; Abstr., 1897, 72, i, 25) describes an experiment in which he treated ethylic acetonedicarboxylate with ethylic succinate in presence of sodium ethoxide and obtained, along with ethylic succinate, a

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bable that the condensation had taken place without the intervention of the ethylic bromide present, the action of sodium ethoxide on ethylic acetonedicarboxylate was examined. 10 grams of ethylic acetonedicarboxylate (1 mol.) were boiled for six hours in a reflux apparatus with a solution of 1.1 gram of sodium (1 at.) in 40 c.c. of alcohol. On addition of water and acidification, a quantity of oil was precipitated which slowly deposited needles of triethylic orcinoltricarb-The yield, 0.5 gram, was only about one-tenth of that theoretically possible. A somewhat larger amount of condensation product is obtained when a smaller proportion of sodium ethoxide is used. In one experiment, 10 grams of ethylic acetonedicarboxylate were boiled with a solution of 0.2 gram of sodium in 30 c.c. of alcohol, and 1 gram of triethylic orcinoltricarboxylate was obtained. The course of the reaction, however, is entirely changed when the proportion of sodium ethoxide is increased. If 3 molecules of the latter are used to every 2 of ethylic acetonedicarboxylate, the lactone C10H10O7 is formed in large quantity, the yield being as good as that obtained by the original method of preparation (Trans., 1897, 71, 1106). The reactions involved in the condensations brought about by sodium ethoxide are no doubt essentially identical with those expressed by the equations quoted in the introduction and in the author's previous paper (loc. cit.) to explain the action of sodium on ethylic acetonedicarboxylate.

As a considerable quantity of triethylic orcinoltricarboxylate was required for the investigation of its constitution, an attempt was made to prepare it in quantity by one or other of the methods recommended by von Pechmann and his pupils. Although it was found that triethylic orcinoltricarboxylate is always formed, both when ethylic acetonedicarboxylate is treated with sodium in the required proportion, and when it is mixed with alcohol, saturated with hydrogen chloride, and allowed to stand; yet the yields obtained were unsatisfactory, being at the best only about 10 per cent. of the theoretical amount. This want of success, which was probably due to some undetected differences in the conditions of the author's experiments and those of von Pechmann, led to the development of other methods for the preparation of the substance.

In an attempt to effect the condensation of ethylic acetonedicarboxylate with ethylic bromacetate by means of zinc, it was observed white, crystalline substance, $C_8H_{10}O_4$, melting at 98°, as well as an acid, $C_7H_6O_4$, a red powder which melted at 186—187°. Triethylic orcinoltricarboxylate melts at 98°, and has the formula $C_{16}H_{20}O_{5}$, just double that quoted by Rimini; so that there is little doubt that the substance $C_8H_{10}O_4$ was triethylic orcinoltricarboxylate. Again, as the lactone $C_{12}H_{10}O_7$ has practically the same percentage composition as the acid $C_7H_6O_4$, melts at 188°, and is often tinged with red when not pure, it is probable that Rimini's so-called acid was in reality the lactone $C_{12}H_{10}O_7$.

that triethylic orcinoltricarboxylate was formed in considerable quantity. A similar condensation takes place when ethylic acetonedicarboxylate is heated at 180° for some hours with about 1 per cent. of its weight of magnesium or iron in the presence of a small quantity of ethylic chloracetate. Of the three metals, magnesium was found to give by far the best results. The ethylic chloracetate acts only by hastening the solution of the metal, for when ethylic acetonedicarboxylate is heated with magnesium alone, condensation takes place as before, although more slowly. In the case of zinc and iron, however, the metal does not bring about the condensation in the absence of ethylic chloracetate. In one experiment, 15 grams of ethylic acetonedicarboxylate were heated with 0.1 gram of magnesium and five drops of ethylic chloracetate at 180° for three hours. The product, an oily liquid which solidified when cold, was digested with cold dilute sulphuric acid to decompose magnesium compounds, and separated from adhering liquid by means of a porous plate. It yielded 5 grams of triethylic orcinoltricarboxylate, that is to say, about 40 per cent. of the yield calculated from the amount of ethylic acetonedicarboxylate employed. Since, however, the yield of condensation product was twice as great as should have been obtained from 0.1 gram of magnesium if the metal acts in the manner attributed to sodium by von Pechmann and his pupils, it follows that either magnesium acts differently from sodium, or that the equations quoted in the introduction as explaining the action of sodium on ethylic acetonedicarboxylate do not account for all the reactions involved. It seems possible that the condensation is due to the following recurring series of transformations. The metallic derivative of ethylic acetonedicarboxylate is first formed, and condenses as shown in the equations forming the metallic derivative of triethylic orcinoltricarboxylate. The latter undergoes double decomposition with more ethylic acetonedicarboxylate, giving free triethylic orcinoltricarboxylate, and regenerating the metallic derivative of ethylic acetonedicarboxylate which is ready to pass again through the same series of transforma-The conclusion that the condensation is due to the recurrence of a series of reactions is borne out by the fact that, when ethylic acetonedicarboxylate is heated at 140° with 1/800 part of its weight of sodium, a 30 per cent. yield of triethylic orcinoltricarboxylate is In one experiment, 4 grams of ethylic acetonedicarboxylate were heated with 5 mgm. of sodium at 140° for two hours; the product, on cooling, solidified, and after digestion with cold, dilute sulphuric acid was collected and separated from adhering liquid by means of a porous plate, 1 gram of triethylic orcinoltricarboxylate being obtained. The weight of sodium required by von Pechmann's equations for the completion of the condensation, on the supposition that 1 atom of the metal is required to every 2 molecules of ethylic acetonedicarboxylate, is approximately one-seventeenth of the weight of ester taken, and one-fifteenth of the theoretical yield of condensation product. Accordingly, in the above experiment, in which the weight of triethylic orcinoltricarboxylate obtained was about two hundred times the weight of the sodium used, the yield is more than thirteen times as great as that indicated by the older theory. That the presence of sodium is necessary to the reaction has been proved by the fact that ethylic acetonedicarboxylate may be heated alone for many hours without the formation of a trace of triethylic orcinoltricarboxylate.

Experiment shows that the yield of triethylic orcinoltricarboxylate is somewhat larger if the proportion of sodium employed is increased, and that it reaches a maximum of about 50 per cent. of the theoretical when ethylic acetonedicarboxylate is heated with 1 per cent. of its weight of sodium exactly in the manner above described. It sinks again to about 40 per cent. when 2 per cent. of sodium is used.

A good yield of triethylic orcinoltricarboxylate is also obtained when ethylic acetonedicarboxylate is heated at about 180° with small quantities of ferric oxide or of the oxides of magnesium and zinc, a fact which is quite in accordance with the above theory.

Formation of Diethylic Hydrogen Orcinoltricarboxylats.

As has been already shown, ethylic acetonedicarboxylate reacts readily with a small quantity of magnesium, yielding triethylic orcinoltricarboxylate. In presence of ethylic chloracetate and of a larger amount of magnesium, the reaction takes a somewhat different course. One of the carboxyethylic groups of the condensation product is hydrolysed by a reaction as yet unexplained, and the magnesium salt of a diethylic hydrogen orcinoltricarboxylate is obtained, from which acids set free the new substance, C14H16O8, as a white solid melting at 141°. This substance is isomeric with the diethylic hydrogen orcinoltricarboxylate, melting at 183-184°, obtained by von Pechmann and Wolman (loc. cit.) by the hydrolysis of triethylic orcinoltricarboxylate. The following method has been found to be the most satisfactory for its 20 grams of pure distilled ethylic acetonedicarboxylate are introduced into a flask of about 150 c.c. capacity, and 5 grams of ethylic chloracetate are added, along with 1 gram of magnesium powder. The flask is fitted with an air condenser, and is heated in a paraffin bath at 180-190°; a vigorous reaction sets in after some time, and a yellowish, gummy solid is slowly deposited. If in the later stage of the operation a quantity of a thick, viscid liquid persistently refuses

to solidify, a little more magnesium must be added. In general, the addition of from 0.1 to 0.2 gram of magnesium suffices for the total conversion of the liquid into the yellowish or brownish solid, which still encloses a little unattacked magnesium. The reaction is usually at an end after about 2 hours heating. After the flask has been removed from the bath and allowed to cool, 50 c.c. of concentrated hydrochloric acid are poured over the solid. The magnesium compound is quickly decomposed, and leaves behind a yellow, flocculent mass of diethylic hydrogen orcinoltricarboxylate, which is collected and washed with a small quantity of water. The product thus obtained is purified by recrystallisation from a large quantity, about a litre, of boiling water. A considerable amount of substance of low melting point remains as an oil floating in the water, and is separated by filtration. As the filtrate cools, diethylic hydrogen orcinoltricarboxylate is deposited in small, granular crystals, and a further quantity may be recovered from the mother liquor by the addition of concentrated hydrochloric acid, the total yield amounting to 5 grams. The product may be further purified by recrystallisation from alcohol or glacial acetic acid, and forms small, opaque, white, stellate clusters when recrystallised from alcohol. It gave the following results on analysis:

The molecular weight was determined by the cryoscopic method. 0.0836 gram in 15.47 grams of glacial acetic acid lowered the freezing point 0.070°. Hence M=300; $C_{14}H_{16}O_8$ requires M=312.

An analysis of the silver salt gave the following result:

0.1907 gave 0.0492 Ag.
$$Ag = 25.8$$
.
 $C_{14}H_{15}AgO_{g}$ requires $Ag = 25.7$ per cent.

Diethylic hydrogen orcinoltricarboxylate is a white, granular powder which melts at 141°, and is easily soluble in alcohol, ether, acetic acid, benzene, or chloroform, less readily soluble in water and light petroleum, and insoluble in concentrated hydrochloric acid. It has an acid reaction, displaces carbon dioxide from alkali carbonates, and is readily precipitated by acids from its solution in alkalis. It gives a bluishviolet colour with ferric chloride in alcoholic solution. The constitution of this substance is fully discussed below (p. 815).

II .- CONSTITUTION OF TRIETHYLIC ORCINOLTRICARBOXYLATE.

Theoretical.

It has been shown by Cornelius and von Pechmann (loc. cit.) that the formation of triethylic orcinoltricarboxylate from ethylic acetonedicarboxylate by the action of sodium may take place in two ways as already indicated (p. 808), and that there are accordingly two possible formulæ for the condensation product:

Hitherto no reaction has been observed in which the two carboxylic groups directly attached to the benzene nucleus show a different chemical behaviour, and accordingly, von Pechmann and Wolman (loc. cit.) concluded that the second or symmetrical formula must be taken provisionally to represent the constitution of triethylic orcinol-tricarboxylate until more definite evidence was forthcoming.

In what follows it is shown that the first, or unsymmetrical, formula must represent correctly the constitution of triethylic orcinoltricarboxylate, for derivatives of two orcinoldicarboxylic acids, both of which have been shown to contain the group 'CH₂·COOH, have been obtained by hydrolysis of triethylic orcinoltricarboxylate and of the diethylic hydrogen orcinoltricarboxylate prepared by heating together magnesium, ethylic chloracetate, and ethylic acetonedicarboxylate. Since in each acid one carboxylic group is definitely known to be in the side chain, the isomerism of the acids must be due to a difference in the position of the second. There are, however, only two possibilities, namely:

Ortho-orcinoldicarboxylic acid.

Para-orcinoldicarboxylic acid.

As the unsymmetrical formula for triethylic orcinoltricarboxylate alone explains the formation of derivatives of these two acids by hydrolysis, the conclusion is drawn that this ester must be represented by formula I.; a view which is strengthened by the fact that, when it is fused with caustic potash, one of the carboxylic groups attached to the benzene nucleus is removed more easily than the other.

The first product obtained when triethylic orcinoltricarboxylate is hydrolysed by caustic alkalis is 2:4-diethylic hydrogen orcinoltricarboxylate,* which has already been described by von Pechmann and Wolman (loc. cit.). It is a monobasic acid which melts at 186-187°, and on being boiled with a solution of hydrogen chloride in alcohol is completely reconverted within two hours into triethylic orcinoltricarboxylate. The free carboxylic group is therefore probably in the side chain, for the other carboxylic groups both lie between carbon atoms of the benzene nucleus which have substituting groups attached to them, and, according to Victor Meyer's law of esterification, should be difficult to esterify by means of alcohol containing hydrogen chloride. The isomeric diethylic hydrogen orcinoltricarboxylate (m. p. 141°), which is produced by the action of magnesium and ethylic chloracetate on ethylic acetonedicarboxylate, is only slowly acted on by alcoholic hydrogen chloride, twenty-four hours being required for its complete conversion into triethylic orcinoltricarboxylate. The free carboxylic group is therefore probably one or other of the two attached directly to the nucleus, and may accordingly occupy either the para- or the ortho-position with respect to the radicle ·CH₂·COOC₂H₅. Since, however, this diethylic hydrogen orcinoltricarboxylate gives, on hydrolysis with aqueous potash, an acid ester, C11H12O6 (m. p. 190°), which will be shown later to be most probably

the free carboxylic group probably occupies the ortho-position, and this substance is accordingly a-4-diethylic hydrogen orcinoltricarboxylate,

The author has been somewhat at a loss to devise a convenient distinctive nomenclature for the isomeric acid esters described in this paper. The following system has been finally adopted. The formula of orcinol is taken as the basis and the seven carbon atoms are denoted in the manner represented in formula I. The positions of the carboxyethylic groups in the acid esters are indicated by prefixing the symbols of the carbon atoms to which they are attached to the name of the compound in question, as is illustrated by formulæ II, III, and IV.

When a-4-diethylic hydrogen orcinoltricarboxylate is hydrolysed with alcoholic potash, one ethyl group is removed, and a monethylic dihydrogen orcinoltricarboxylate (m. p. 198°) is formed. This substance is a dibasic acid, which, after one hour's boiling with alcoholic hydrogen chloride, is completely converted into the a-4-diethylic hydrogen orcinoltricarboxylate from which it was prepared. Accordingly, the carboxyethylic group in the side chain must have been hydrolysed, and the new substance is 4-monethylic dihydrogen orcinoltricarboxylate,

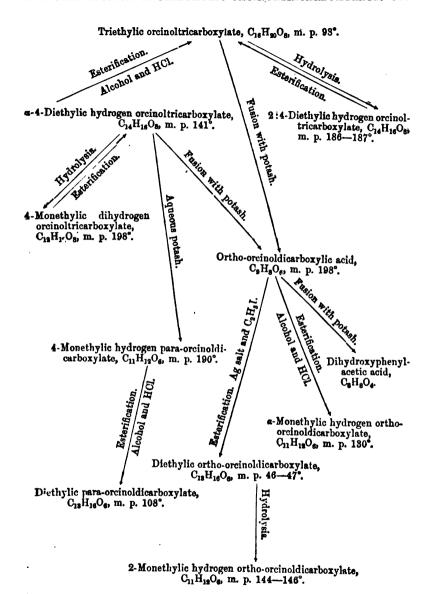
When either triethylic orcinoltricarboxylate or a-4-diethylic hydrogen orcinoltricarboxylate is fused with caustic potash for about 15 minutes, orcinolmonocarboxylic acid (3:5 dihydroxyphenylacetic acid), which has already been fully described by von Pechmann and his pupils (Ber., 1886, 19, 1446; 1898, 31, 2014), is the sole product. If, however, the fusion is carried out at a low temperature, and for a much shorter time, an orcinoldicarboxylic acid is obtained. This substance has the formula C₀H₈O₆, melts at 198°, and gives a silver salt, C9H6Ag2O6. When it is boiled with alcoholic hydrogen chloride for an hour, one ethyl group only enters the molecule, and even on long continued boiling the second carboxylic group does not seem to be The acid ester, C₁₁H₁₂O₆, thus obtained melts at 130°, and must have its carboxyethylic group in the side chain. The corresponding diethylic ester may be made by heating the silver salt of the acid with ethylic iodide, and is a solid, C18H16O6, melting at 46-47°. The diethylic ester, when hydrolysed by caustic potash, yields an acid ester, C₁₁H₁₂O₆, melting at 144-146°, which is isomeric with that just described, and must have its ethylic group attached to the carboxylic group in the nucleus. The presence of the group 'CH2' COOH in the dicarboxylic acid, CoHsO6 (m. p. 198°) is proved by the fact that the acid forms an intermediate product in the preparation of dihydroxyphenylacetic acid, C₆H₈(OH₂)·CH₂·COOH, and also by the fact that one of its carboxylic groups is so easily esterified. There are, however, two possible formulæ for this acid derivable from the unsymmetrical formula for triethylic orcinoltricarboxylate,

It will be shown later that two other substances—a monethylic hydrogen orcinoldicarboxylate, C₁₁H₁₂O₆, melting at 190°, isomeric with those just described, and containing only one carboxylic group attached directly to the nucleus, and a diethylic orcinoldicarboxylate, C18H16Oa, melting at 108°—have been prepared from a-4-diethylic hydrogen orcinoltricarboxylate; these melt many degrees higher than the corresponding derivatives of the dicarboxylic acid melting at 198°. This relationship resembles that existing between the similarly constituted homophthalic and homoterephthalic acids, which melt at 175° and 237—238° respectively. Until better evidence is forthcoming, it must be assumed that the acid which gives derivatives melting at the lower temperatures is a 3:5-dihydroxyhomophthalic acid, and that the isomerides of higher melting point are derivatives of 3:5-dihydroxyhomoterephthalic acid. For convenience, and to show the close connection between these acids and orcinol, they are called in what follows ortho-orcinoldicarboxylic acid and para-orcinoldicarboxylic acid respectively. The scheme on p. 818 shows the constitutional formulæ attributed to the compounds just described.

When a-4-diethylic hydrogen orcinoltricarboxylate is hydrolysed with dilute aqueous potash, the acid ester, $C_{11}H_{12}O_6$, melting at 190° is formed. This substance is easily esterified by alcoholic hydrogen chloride, giving a diethylic orcinoldicarboxylate, $C_{13}H_{16}O_6$, which melts at 108°. The acid ester must accordingly contain the group $-CH_2$ ·COOH, and, since, for the reason already given, it is assumed to be a derivative of para-orcinoldicarboxylate, as shown in the scheme on p. 818. The diethylic ester, $C_{13}H_{16}O_6$, melting at 108° , must accordingly be diethylic para-orcinoldicarboxylate. An attempt was made to prepare para-orcinoldicarboxylate. An attempt was made to prepare para-orcinoldicarboxylic acid by hydrolysing the acid ester, $C_{11}H_{12}O_6$ (m. p. 190°), but without success; the hydrolysis could not be effected without the simultaneous loss of carbon dioxide, and in consequence the only product obtained was dihydroxyphenylacetic acid.

The diagram on p. 819 shows the relationship between the substances described in this part of the paper.

CH ₂ ·COOC ₂ H ₅ HOCOC ₃ H ₅	CH ₂ ·COOC ₂ H ₅ H HO OH COOC ₂ H ₅ Diethylic para-orcinoldi- carboxylate, m. p. 108°.
CH ₂ ·COOH HOCOC ₂ H ₅ HOCOC ₂ H ₅ 2-Monethylic hydrogen ortho-orcinol-dicarboxylate, m. p.	CH ₂ ·COOH HOOOT COOC ₂ H ₅ 4-Monethylic hydrogen para-oreinoldicarboxylate, m.p.
CH ₂ ·COOC ₂ H ₅ H COOH HO A-Monethylic hydrogen ortho-oreinoldicarboxylate, m. p. 180°.	CH ₂ ·COOC ₂ H ₅ HOOOH COOH (Not isolated.)
CH ₂ ·COOH HO HO Ortho-oreinoldicarboxylic scid (8: 6-dihydroxy- homophthalic scid), m. p. 198°.	CH ₂ ·COOH H HO OH COOH Para-oreinoldicarboxylic acid (8:5-dihydroxy- homotersphthalic acid). (Not isolated.)
CH ₂ ·COOH H COOH H H H COOH H Omophthalic soid, m. p. 176°.	CH ₂ ·COOH H H H COOH COOH Tomoterephthalic acid, m. p. 287-288°.



Experimental.

The materials used in this part of the investigation were triethylic orcinoltricarboxylate as prepared by any of the methods described in Part I, and a-4-diethylic hydrogen orcinoltricarboxylate made by

the action of magnesium on ethylic acetonedicarboxylate in presence of ethylic chloracetate.

Hydrolysis of Triethylic Orcinoltricarboxylats; 2:4-Diethylic Hydrogen Orcinoltricarboxylate.

This substance is best made by boiling triethylic orcinoltricarboxylate with about three times its weight of caustic potash in alcoholic solution for two or three minutes, diluting with water, and acidifying with sulphuric acid. The white precipitate which is formed crystallises well from acetic acid in plates sometimes four or five millimetres across, or from alcohol in rhombohedra, melts at 186—187°, and is identical with the ester, melting at 183—184°, which von Pechmann and Wolman (loc. cit.) obtained by allowing triethylic orcinoltricarboxylate to remain for two days in solution in dilute aqueous caustic soda.

When boiled for two hours with ten times its weight of alcohol containing 3 per cent. of hydrogen chloride, it gave a nearly quantitative yield of triethylic orcinoltricarboxylate, crystallising from dilute alcohol in needles melting at 97°.

Esterification of a-4-Diethylic Hydrogen Orcinoltricarboxylate.

An attempt to esterify this substance by boiling it for two hours with 3 per cent. alcoholic hydrogen chloride was unsuccessful, and the ester was accordingly prepared from the silver salt by interaction with ethylic iodide. A quantity of the silver salt was heated with excess of ethylic iodide in a sealed tube immersed in boiling water; after two hours, the product was washed out with alcohol and filtered from silver iodide. The solution, when concentrated on the water-bath, deposited two crops of crystals, the first of which melted at 141°, and consisted of unchanged a-4-diethylic hydrogen orcinoltricarboxylate, whilst the second, after recrystallisation from dilute alcohol, melted at 97°, and showed all the properties of triethylic orcinoltricarboxylate.

As a second experiment showed that complete esterification might be effected by long-continued boiling with alcoholic hydrogen chloride, a quantity of the α -4-diethylic ester was added to 20 times its weight of 3 per cent. alcoholic hydrogen chloride, and the whole boiled on the water-bath in a reflux apparatus. After six hours, a small quantity of the liquid was withdrawn, and on dilution with water, a crystalline substance separated which, when heated, softened at 90°, but did not melt completely below 115°. After 24 hours the substance precipitated by addition of water melted completely

below 90°; the operation was therefore stopped at this stage, and the contents of the flask after filtration were diluted with water, needle-shaped crystals being deposited, which after recrystallisation melted at 97°, and consisted of triethylic orcinoltricarboxylate.

Hydrolysis of a-4-Diethylic Hydrogen Orcinoltricarboxylate; 4-Monethylic Dihydrogen Orcinoltricarboxylate.

Three grams of a-4-diethylic hydrogen orcinoltricarboxylate were dissolved in 20 c.c. of alcohol, and after addition of a solution of 12 grams of caustic potash in 50 c.c. of alcohol, the mixture was boiled on the water-bath. For a short time, the liquid remained perfectly clear, and then suddenly deposited a dense, crystalline precipitate of potassium 4-monethylic orcinoltricarboxylate. Water was added until the whole had dissolved, and then dilute sulphuric acid in excess; the crystals, which separated, were collected, and the mother liquor was extracted with ether. In all, 2.4 grams of the product were obtained, and after recrystallisation from hot water,

0.1290 gave 0.2397 CO_2 and 0.0490 H_2O . C = 50.67; H = 4.22. $C_{12}H_{12}O_8$ requires C = 50.70; H = 4.23 per cent.

The silver salt was also prepared and analysed.

0.1277 gave 0.0546 Ag. Ag = 42.8. $C_{12}H_{10}Ag_2O_8$ requires Ag = 43.4 per cent.

4-Monethylic dihydrogen orcinoltricarboxylate melts at 198° with evolution of gas, and gives a deep purple colour with ferric chloride in alcoholic solution. It is soluble in alcohol, ether, glacial acetic acid, or hot water, but only sparingly in chloroform, and is almost insoluble in benzene. From glacial acetic acid, it crystallises in large, thin plates, which contain 1 mol. of acetic acid of crystallisation; the crystals, however, give off acetic acid when exposed to air, and lose their lustre completely. In order to determine the amount of acetic acid present, a quantity of the crystals was dried as rapidly and completely as possible on a porous plate; one portion, thus obtained, was heated in an air-bath at 140° for half-an-hour, whilst a second portion was exposed to air for four days, and then heated at 140° for the same period.

0.0970, quickly dried, lost 0.0164 acetic acid at 140°. $C_2H_4O_2 = 16.9$. 0.0993, after four days exposure, lost 0.0013 acetic acid at 140°. $C_2H_4O_2 = 1.3$. $C_{12}H_{12}O_2 + C_2H_4O_2$ requires $C_2H_4O_2 = 17.9$ per cent.

One gram of 4-monethylic dihydrogen orcinoltricarboxylate was boiled for two hours with 20 grams of a 3 per cent, solution of hydrogen

chloride in alcohol in a reflux apparatus. The liquid when cold deposited 0.65 gram of a crystalline substance, which melted at 141° and was a-4-diethylic hydrogen orcinoltricarboxylate.

Ortho-orcinoldicarboxylic Acid.

When either triethylic orcinoltricarboxylate or a-4-diethylic hydrogen orcinoltricarboxylate is fused for a short time with caustic potash dissolved in a little water, the chief product of the reaction is ortho-orcinoldicarboxylic acid. Since the fusion is carried out in exactly the same way with both substances, the preparation of the new acid from triethylic orcinoltricarboxylate is alone described.

A solution of 13 grams of caustic potash in 10 grams of water in a nickel crucible is kept at 120° by a small flame, 4 grams of triethylic orcinoltricarboxylate are quickly introduced, and the mixture vigorously stirred. Violent effervescence takes place at first owing to the escape of alcohol vapour, but in a short time dies down; after four minutes, the product is cooled, water and dilute sulphuric acid are added, and the whole is extracted with ether. A solid substance is thus obtained mixed with a small amount of a syrup, which may be removed by spreading on a porous plate. The syrup, which is very readily soluble in water, probably contains dihydroxyphenylacetic acid, produced by the further action of the caustic potash on some of the ortho-orcinoldicarboxylic acid. About 1.5 grams of the new acid are obtained; it crystallises well from water in flat needles which contain 1H₂O.

0.1545 gave 0.2656 CO_2 and 0.0611 H_2O . C = 46.88; H = 4.39. 0.5828, at 110°, lost 0.0460 H_2O . $H_2O = 7.89$.

 $C_9H_8O_6 + H_2O$ requires C = 46.96; H = 4.04; $H_2O = 7.82$ per cent. 0.1267 anhydrous acid gave 0.2355 CO_2 and 0.0465 H_2O . C = 50.69; H = 4.06.

 $C_9H_8O_6$ requires C=50.94; H=3.77 per cent.

The silver salt of the acid was prepared and analysed.

0.5040 gave 0.2540 Ag. Ag = 50.4. $C_0H_0Ag_0O_0$ requires Ag = 50.7 per cent.

Ortho-orcinoldicarboxylic acid melts at 198° with evolution of gas. It has a strongly acid taste, is moderately soluble in cold, but easily so in boiling, water, and dissolves readily in acetic acid or alcohol. Its alcoholic solution gives, with ferric chloride, a deep blue coloration, which, on addition of water, assumes a purple tinge,

Ethylic Ortho-orcinoldicarboxylates.

a-Monethylic Hydrogen Ortho-orcinoldicarboxylate.—0.35 gram of ortho-orcinoldicarboxylic acid was boiled for an hour with 10 grams of a 3 per cent. alcoholic solution of hydrogen chloride in a reflux apparatus. The liquid was then evaporated on the water-bath, and the crystalline solid which remained was crystallised from chloroform.

0.1361 gave 0.2742 CO_2 and 0.0609 H_2O . C = 54.93; H = 4.97. $C_{11}H_{12}O_6$ requires C = 55.00; H = 5.00 per cent,

a-Monethylic hydrogen ortho-orcinoldicarboxylate melts at 130°, shows a marked acid reaction with litmus, and dissolves in sodium hydrogen carbonate solution with vigorous effervescence. It is easily soluble in alcohol or chloroform, but only slightly so in hot benzene, and is insoluble in cold water or light petroleum. It seems to be quickly hydrolysed by boiling water, as it apparently dissolves, but does not separate out again when the water is cooled. With ferric chloride in alcoholic solution, it gives a purple coloration.

Diethylic Ortho-orcinoldicarboxylate.—Only one of the two carboxylic groups in ortho-orcinoldicarboxylic acid is esterified even after long continued boiling with alcoholic hydrogen chloride. The diethylic ester, however, was easily obtained by heating a quantity of the silver salt with an excess of ethylic iodide in a sealed tube at 100°. The product was washed out of the tube with alcohol, filtered from silver iodide, and concentrated on the water-bath; an oily liquid remained behind which, after a considerable time, solidified. found that this solid contained a considerable quantity of 2-monethylic hydrogen ortho-orcinoldicarboxylate, and accordingly it was boiled with 3 per cent. alcoholic hydrogen chloride for half an hour, in order to convert the latter completely into the diethylic ester. evaporation of the alcohol, a solid mass of diethylic ortho-orcinoldicarboxylate remained, and this was recrystallised from dilute alcohol, from which it separated in fine needles.

0.1094 gave 0.2347 CO_2 and 0.0587 H_2O . C = 53.51; H = 5.96. $C_{18}H_{16}O_6$ requires C = 58.21; H = 5.97 per cent.

Diethylic hydrogen ortho-orcinoldicarboxylate melts at 46—47°, and is easily soluble in alcohol or ether, but insoluble in water. It gives a faint purple colour with ferric chloride in alcoholic solution, and does not dissolve in sodium hydrogen carbonate solution.

2-Monsthylic Hydrogen Ortho-orcinoldicarboxylate.—0.4 gram of diethylic ortho-orcinoldicarboxylate was boiled with about 15 c.c. of dilute caustic soda solution (1 in 10) for two minutes, and was then mixed with

excess of dilute sulphuric acid. A bulky precipitate consisting of slender needles appeared, which was collected and recrystallised by dissolving in hot acetic acid and adding water until a slight turbidity appeared. After 12 hours, the greater part of the substance had crystallised out in long, prismatic needles.

0.1464 gave 0.2952 CO_2 and 0.0664 H_2O . C = 54.99; H = 5.04. $C_{11}H_{12}O_6$ requires C = 55.00; H = 5.00 per cent.

2-Monethylic hydrogen ortho-orcinoldicarboxylate melts at 144—146°, and dissolves readily in alcohol or acetic acid, but is insoluble in water. Its alcoholic solution gives, with ferric chloride, a faint green colour, which changes to a faint purple on addition of water.

Ethylic Para-oroinoldicarboxylates.

4-Monethylic Hydrogen Para-orcinoldicarboxylate.—When a-4-diethylic hydrogen orcinoltricarboxylate is boiled with dilute aqueous caustic potash for a short time, 4-monethylic hydrogen para-orcinoldicarboxylate is the chief product. 3 grams of a-4-diethylic hydrogen orcinoltricarboxylate were boiled with a solution of 15 grams of caustic potash in 50 c.c. of water for five minutes. After acidification with dilute sulphuric acid, the solution was extracted with ether, and a solid substance was obtained which was drained from adhering syrup on porous plates, and recrystallised from water, the yield amounting to 1 gram. The product crystallises from water with 1H₂O, which is given off at 100°.

0.1489 gave 0.2755 CO₂ and 0.0724 H₂O. C = 50.67; H = 5.40.

 $0.2488 \text{ lost } 0.0184 \text{ H}_2\text{O} \text{ at } 110^\circ$. $\text{H}_2\text{O} = 7.4$.

 $C_{11}H_{12}O_6 + H_2O$ requires C = 51.16; H = 5.42; $H_2O = 7.0$ per cent. 0.1310 anhydrous substance gave 0.2626 CO_2 and 0.0600 H_2O . C = 54.66; H = 5.09.

 $C_{11}H_{19}O_6$ requires C = 55.00; H = 5.00 per cent.

The silver salt was also made and analysed.

0.1897 gave 0.0588 Ag. Ag = 31.00.

 $C_{11}H_{11}AgO_6$ requires $Ag = 31\cdot10$ per cent.

4-Monethylic hydrogen para-orcinoldicarboxylate melts at 190° and is soluble in water, ether, alcohol, glacial acetic acid, or acetone, but insoluble in chloroform, light petroleum, or benzene. In alcoholic solution, it gives a purple colour with ferric chloride.

Disthylic Para-orcinoldicarboxylats.—4-Monethylic hydrogen paraorcinoldicarboxylate was boiled for two hours with 3 per cent. alcoholic hydrogen chloride; the alcohol was then evaporated off, and the solid

residue recrystallised from boiling water, in which it was only slightly soluble. As the solution cooled, the product separated in long, thin needles.

0.1229 gave 0.2614 CO_2 and 0.0672 H_2O . C = 58.01; H = 6.08. $C_{18}H_{16}O_6$ requires C = 58.21; H = 5.97 per cent.

Diethylic para-orcinoldicarboxylate melts at 108°, has no action on sodium hydrogen carbonate solution, and dissolves readily in alcohol, but only sparingly in boiling water, being almost insoluble in cold. It gives a brown colour with ferric chloride in alcoholic solution.

THE OWENS COLLEGE,
MANCHESTER.

LXXVIII.—The Colouring Matter of Cotton Flowers, Gossypium Herbaceum. Note on Rottlerin.

By ARTHUR GEORGE PERKIN, F.R.S.E.

Among the various portions of the cotton plant which have been industrially employed must be included the flowers which constitute one of the numerous Indian dye stuffs. According to Watt (Dictionary of the Economic Products of India), they are thus utilised in the Manipur district, although the information on the subject Wardle, in his report, on the "Dyes and Tans of India," states that from these flowers he obtained shades which ranged from bright yellow, greenish-yellow, and fawn colour, to orange-, reddish-, and brownish-yellow. He considered them to be rich in colouring matter, and as a dye-stuff to possess much the same properties as the flowers of Butea frondosa. As is well known, colouring matter is present in other portions of the plant, the seeds containing a somewhat feeble yellow dye which, by the action of acids, is converted into the so-called "cotton seed blue" (Kuhlmann, Compt. rend., 1861, 53, 444). This has been further examined by L. Marchlewski (Die Chemie des Gossypöls, Anzeiger der Akademie der Wissenschaften in Krakau, November, 1897). It is not identical, and does not appear to be closely allied, with that present in the flowers, but, on the other hand, a dye exists in the bark [Wayne (1872) and Staehle (1876), compare Watt's Dictionary | which has points of resemblance with the gossypetin described in this paper.

For the supply of raw material (3 lbs.), I am indebted to the authorities of the Imperial Institute. This yielded approximately 1 per cent. of crude colouring matter, and, after purification, only 10 grams of the pure substance remained for investigation.

EXPERIMENTAL.

The colouring matter was present in the flowers almost entirely as glucoside, and the following process was adopted for its isolation. The flowers were thoroughly extracted with boiling alcohol, the extract evaporated to a small bulk, treated with water, and the mixture extracted with ether to remove chlorophyll and wax, which were present in some quantity. The brown, aqueous solution containing the glucoside was digested for half an hour with a little sulphuric acid at the boiling point, and, on cooling, a flocculent, greenish-yellow precipitate of the crude colouring matter separated, which was collected and drained on a porous tile. It was now dissolved in a little alcohol, the solution poured into ether, causing the separation of a tarry product, which was removed, and the clear liquid repeatedly washed with water until the washings were no longer After evaporation to dryness, a pale yellow residue remained, which was crystallised from dilute alcohol. For analysis, the product was converted into the acetyl derivative, which, after purification, was hydrolysed with sulphuric acid in the usual manner.

0.1080, dried at 160°, gave 0.23 CO_2 and 0.0335 H_2O . C = 58.07; H = 3.44.

 $C_{16}H_{12}O_8$ requires C = 57.83; H = 3.61 per cent.

This substance is a new colouring matter, for which the name gossypetin is proposed; it forms glistening, yellow needles, closely resembling quercetin in appearance, and is readily soluble in alcohol, but only very sparingly in water. Concentrated alkaline solutions dissolve it, forming orange-red solutions, which, on agitation and dilution with water, become green, and finally assume a dull brown tint. Ammonia behaves very similarly, and these reactions recall those given by myricetin, $C_{15}H_{10}O_8$, in an analogous manner (Trans., 1896, 69, 1287); the formula also suggested that gossypetin might be a myricetin monomethyl ether, but this was disproved, as it does not contain a methoxy-group. Alcoholic lead acetate gave a deep red precipitate in the cold, passing into dull brown at the boiling point, and alcoholic ferric chloride a dull, olive-green liquid. Sulphuric acid dissolves it, forming an orange-red solution.

Gossypetin Sulphate.—The addition of sulphuric acid to gossypetin suspended in boiling acetic acid produced an orange liquid which gradually deposited crystals; these were collected and washed with acetic acid.

0.1279 gave 0.2093 CO_2 and 0.0360 H_2O . C=44.63; H=3.13. $C_{16}H_{12}O_3H_3SO_4$ requires C=44.65; H=3.25 per cent,

The compound consisted of glistening, orange-red needles, and was decomposed by treatment with water into gossypetin and sulphuric acid.

The hydrochlorids, similarly prepared, forms orange needles, but, being slowly decomposed at 100°, could not be analysed. The hydriodids, obtained as fine, orange-red needles, was, however, more stable.

0.0991 gave 0.1543 CO_2 and 0.0300 H_2O . C=42.46; H=3.36. $C_{16}H_{12}O_8$, HI requires C=41.74; H=2.83 per cent.

Monopotassium gossypstim is formed when potassium acetate is added to a boiling alcoholic solution of the colouring matter; an orange-yellow precipitate at once separates, which, on standing, assumes a dull green tint, evidently due to oxidation. It was rapidly collected and washed with alcohol.

0.2156 gave 0.0503 K_2SO_4 . K = 10.46. $C_{16}H_{11}O_8K$ requires K = 10.54 per cent.

The salt is a crystalline powder insoluble in cold absolute alcohol, and only very sparingly soluble in water. When digested with boiling water, an orange-brown solution is obtained, which quickly deposits a yellow precipitate of gossypetin; it thus behaves in an analogous manner to the salts of quercetin, fisetin, &c., previously described (this vol., 433). As shown in this communication, the above reaction is a strong indication that the colouring matter contains hydroxyl groups in relatively ortho-positions, and there is little room for doubt that the molecular weight of gossypetin corresponds with that required for the formula $C_{16}H_{12}O_8$.

Hexacetylgossypetin.—The employment of sodium acetate in the acetylation of gossypetin was not beneficial, and the colouring matter was therefore digested with boiling acetic anhydride alone for 6 hours; the addition of alcohol caused a separation of crystals, which were collected and digested with a fresh quantity of the anhydride for 3 hours. The product was crystallised from a mixture of alcohol and acetic acid.

0.1185 gave 0.2482 CO₂ and 0.0463 H₂O. C = 57.12; H = 4.34. $C_{16}H_6O_8(C_2H_8O)_6$ requires C = 57.53; H = 4.11 per cent.

It forms colourless needles melting at 222—224°, and is readily soluble in acetic acid, but somewhat sparingly so in alcohol. The acetyl groups were estimated by hydrolysing the compound with sulphuric acid in the usual manner.

0.6923 gave 0.3910 $C_{16}H_{12}O_8$. Found, 56.48. $C_{16}H_6O_8(C_2H_8O)_6$ requires $C_{16}H_{12}O_8 = 56.84$ per cent.

Fusion with Alkali.—When gossypetin is fused with caustic potash at 200—220°, two crystalline decomposition products are obtained,

melting at 210° and at 194—196° respectively; these consisted of phloroglucinol and protocatechnic acid.

Dyeing Properties.—On wool mordanted with aluminium, tin, chromium, and iron compounds, gossypetin gave the following shades, indicating that it is a new colouring matter:

Aluminium. Tin. Chromium. Iron.
Pale orange-brown. Orange-red. Dull brown. Deep, dull olive.

With an aluminium mordant, the results vary greatly, according as chalk is present or absent in the dye-bath, a result evidently due to the ready oxidation of gossypetin in the presence of alkalis or alkaline earths. Thus, if the mordanted wool, which is of an acid nature, is employed alone, the above shade is produced; but if chalk is added, a deep olive-yellow is obtained. Calico mordanted with aluminium, being of a basic nature, yields this olive-yellow shade without the employment of chalk; the addition of acetic acid to the bath prevents oxidation, however, and an orange-brown colour is produced.

The dyeing properties of the flowers are very distinct from those of gossypetin; this is due to the fact that they contain the glucoside, and not the free colouring matter. The following shades were obtained:

Aluminium. Tin. Chromium. Iron.
Dull yellow. Orange-brown. Dull brown-yellow. Dull olive.

In this case, it was not possible to produce a greener shade on the aluminium mordant, the glucoside being less prone to exidation than the colouring matter. No marked tinctorial resemblance was observed between the cotton and Butea flowers, as stated by Wardle (loc. cit.), and their respective colouring matters, gossypetin and butein (Hummel and Cavallo, Proc., 1893, 10, 11), have little apparent chemical relationship.

The properties of gossypetin show that it is either a member of, or belongs to a group closely allied with the quercetin or flavone series of colouring matters. From a consideration of this point, and the fact that it contains six hydroxyl groups, two of which are in the ortho-position relatively to one another, and also a catechol and phloroglucinol nucleus, the following constitution suggests itself as possible:

Further work on this colouring matter will be carried out when a

fresh supply of raw material is available; this, unfortunately, is not readily procured.

During the course of the investigation, my attention was drawn to thujetin, the yellow colouring matter of Thuja occidentalis (Arbor vitæ), first isolated by Kawalier (Jahresb., 1858, 512), and subsequently examined by Rochleder (Mitt. aus. dem chemischen Laboratorium zu Prag, 10, Feb. 11, 1858). The analyses of thujetin, dried at 100° , are in agreement with the formula $C_{16}H_{12}O_8 + H_2O$, and the general properties of this substance are similar to those of gossypetin. To determine if the substances were identical, some quantity of the plant was procured, but, unfortunately, this was of a poor character for the purpose, as from 500 grams only 0.05 gram of thujetin could be isolated; sufficient, however, was obtained to prove that it was not gossypetin, for the acetyl derivative melted at $205-206^{\circ}$. It is more probable, therefore, that thujetin is identical with myricetin, and this point will be further studied.

Note on Rottlerin.

In previous communications (Trans., 1893, 63, 981; 1895, 67, 230), it was found that rottlerin, a colouring matter of kamala (Mallotus Phillipinensis) yields acetic and benzoic acids on fusion with alkali. As nitric acid gives ortho- and para-nitrocinnamic acids, this result appeared to be due to the decomposition of a cinnamyl nucleus. The formula of rottlerin deduced from analyses of its mono-substitututed salts is, or closely approximates to, $C_{88}H_{30}O_{9}$, and it moreover contains hydroxyl groups. As the former results in no way accounted for the presence of these groups, and as larger quantities of the colouring matter were now available, its behaviour with fused alkalis was studied at a higher temperature, namely, 220—240°. The products, isolated in the usual manner, consisted of acetic and benzoic acids, together with phloroglucinol, which melted at 210°, and on analysis gave the following result:

0.0952 gave 0.1998 CO₂ and 0.041 H₂O. C = 57.23; H = 4.78. $C_6H_6O_8$ requires C = 57.14; H = 4.76 per cent.

The formation of mono-substituted salts of rottlerin led to the suggestion that a carboxyl group was present in the compound (loc. cit.), but this now seems doubtful, as numerous phenolic colouring matters in which this group is absent (this vol., 433) have been found to possess a similar property.

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LXXIX.—The Colouring Matters contained in Dyer's Broom (Genista tinctoria) and Heather (Calluna vulgaris).

By ABTHUR GEORGE PERKIN, F.R.S.E., and FREDERICK GEORGE Newbury.

In addition to the well known natural dyestuffs now found in commerce, numerous other plants were formerly employed in Europe for dyeing purposes; as some of these have not been previously studied, it was of interest to submit them to examination, and an account is here given of the colouring matter of dyer's broom and heather.

I. DYER'S BROOM.

Genista tinctoria (dyer's broom, dyer's greenweed; genet, genestrole, trentanel, Fr.; Ginster, Germ.) is found in the pastures, thickets, and waste places throughout Central and Southern Europe, across Russian Asia to the Baikal, and northward to Southern Sweden. It is frequent in the greater part of England, but rare in Ireland and Scotland. Although not previously studied, the fact that it contains a yellow colouring matter is recorded by numerous writers, and the following embody the principal references to the dyeing and general properties of the plant: Bancroft (Philosophy of Permanent Colours, 1813, 2, 108), Gmelin (Handbook of Chemistry, 16, p. 517), Berthelot (On Dyeing, 1824, 2, p. 242), Gonfreville (Art de la teinture de laines, p. 501), Leuchs (Farben u. Farbekunde, 1846, 2, 309), and Schutzenberger (Traite de matières colorantes, 1867, 4, 422). The following interesting statement occurs in Kane's Elements of Chemistry (1849, p. 933), and no doubt owes its origin to the very similar dyeing properties of both plants: "Luteolin is the colouring matter of the weld, and probably of the dyer's broom."

For purposes of extraction, the plant is best cut into small pieces; it should not be ground, for in this condition it is converted by hot water into a viscous mass extremely difficult to manipulate. Quantities of 1 kilo. at a time were digested for 6 hours with 10 kilos. of boiling water, the extract treated with 10 c.c. of glacial acetic acid, and then with excess of lead acetate solution. A pale yellow, viscous precipitate separated, and this was collected and washed with water, the filtrate A being reserved for examination. The product, made into a thin cream with water, was decomposed by boiling dilute sulphuric acid, the lead sulphate removed, and the filtrate allowed to cool; the dull yellow precipitate which separated was collected, dissolved in a little alcohol and poured into ether, which caused the separation of a

dark coloured, resinous substance; this was removed, and the clear liquid washed with water until the washings were colourless. On evaporating the ether, a yellow, crystalline mass remained containing two substances, one yellow, B, and the second, C, colourless or nearly so. The latter, being more soluble, could be partially removed by fractional crystallisation from dilute alcohol, and this process was resorted to at first, but subsequently advantage was taken of the fact that B with sulphuric acid, in the presence of acetic acid, forms a sparingly soluble sulphate, whilst C does not react with the acid and remains in solution.

The sulphate of B was collected, washed with acetic acid, decomposed by water, and the regenerated colouring matter crystallised from dilute alcohol.

0.1091 gave 0.2526 CO₂ and 0.0381 H₂O. C = 63.14; H = 3.87. $C_{15}H_{10}O_6$ requires C = 62.93; H = 3.50 per cent.

It was obtained in glistening, yellow needles, readily soluble in alcohol, and soluble in alkali solutions with a yellow coloration. With alcoholic lead acetate, a yellow precipitate was formed, and alcoholic ferric chloride yielded first a green and then a brownish-red coloration. Potassium acetate, in the presence of alcohol, gave a gelatinous precipitate of a potassium salt too soluble for examination.

Tetracetyl Compound.—When the substance B was digested with acetic anhydride and sodium acetate in the usual manner, an acetyl compound was obtained, crystallising from alcohol, in which it was very sparingly soluble, in colourless needles melting at 221—223°.

0.123 gave 0.273 CO₂ and 0.046 H₂O. C = 60.52; H = 4.15. $C_{15}H_6O_6(C_2H_3O)_4$ requires C = 60.79; H = 3.96 per cent.

The acetyl groups were estimated by hydrolysis with sulphuric acid.

0.8665 gave 0.551 $C_{15}H_{10}O_6$. Found, 63.58. $C_{15}H_6O_6(C_2H_8O)_4$ requires $C_{15}H_{10}O_6 = 63.00$ per cent.

On fusion of the substance B with alkali at 220°, phloroglucinol (m. p. 210°) and protocatechnic acid (m. p. 194—196°) formed the main products of the decomposition.

These results suggested that the colouring matter $C_{15}H_{10}O_6$ was identical with the luteolin of weld, and its acid compounds were examined, for it has been shown by one of us (Trans., 1896, 69, 208) that, whereas the sulphate and hydriodide of luteolin have the formulæ $C_{15}H_{10}O_6,H_2SO_4$ and $C_{15}H_{10}O_6,HI$ respectively, the hydrochloride and hydrobromide are peculiar in crystallising with $1H_2O$, and differ in this respect from the acid compounds of all other yellow colouring matters at present examined.

The sulphate formed orange-red needles, rapidly decomposed by water.

0.1332 gave 0.2285 CO₂ and 0.0345 H₂O. C = 46.78; H = 2.87. $C_{15}H_{10}O_6,H_2SO_4$ requires C = 46.87; H = 3.12 per cent.

The hydriodide was obtained in glistening, orange plates.

0.1304 gave 0.2065 CO_2 and 0.0308 H_2O . C=43.18; H=2.62. $C_{15}H_{10}O_6$, HI requires C=43.47; H=2.65 per cent.

The hydrochloride was an ochre-coloured mass of fine needles, and, as is the case with luteolin, an excess of acid was necessary for its formation. It is decomposed by water somewhat slowly.

0.1137 gave 0.2177 CO_2 and 0.0325 H_2O . C = 52.30; H = 3.17. $C_{15}H_{10}O_6$, $HCl + H_2O$ requires C = 52.70; H = 3.81 per cent.

These reactions prove without doubt that the colouring matter $C_{15}H_{10}O_6$ of the *Genista tinctoria* is *luteolin*, and a comparison of its dyeing properties with those of luteolin prepared from weld (*Reseda luteola*) further corroborated this fact. Woollen cloth mordanted with chromium, aluminium, tin, and iron compounds was employed, and the shades, which have not been described previously, are given, together with those of quercetin, for the sake of comparison.

Chromium. Aluminium. Tin. Iron.

Luteolin.. Brown-orange. Orange-yellow. Bright yellow. Blackish-olive.

Quercetin Red-brown. Brown-orange. Bright orange.

The yield of luteolin by the above method was small, 1000 grams of the plant giving only 3.7 grams of the crude substance, which was reduced to about 2.8 grams on purification. It is interesting to note that, previously, luteolin has only been known to occur in weld.

The More Soluble Colouring Matter.

The substance C (page 831) contained in the dilute alcoholic mother liquors from the purification of the luteolin was also present in considerable quantity in the filtrate (A) from the lead precipitate, from which it was isolated as follows. To the boiling liquid, ammonia was added, causing the separation of a voluminous lemon-yellow precipitate, which was collected, washed with water, and decomposed with boiling dilute sulphuric acid. The clear liquid, decanted from the lead sulphate, was extracted with ether, and the extract evaporated, leaving a brownish, crystalline mass, which was washed on the pump, first with water, then with dilute alcohol, and dried. The crude product isolated by these methods was dissolved in boiling acetic acid, the brown solution treated with animal charcoal, and evaporated to a

small bulk; when left overnight, a semi-solid mass of needles separated, which was collected, washed with a little acetic acid, and then with water. With the object of removing any traces of luteolin, a small quantity of lead acetate was added to an alcoholic solution of the product, and the filtrate, after the addition of acetic acid, was evaporated to a small bulk and diluted with boiling water. The long, glistening needles which separated on cooling had still a faint brown tint, and to remove this the compound was converted into its acetyl derivative, which, after purification, was hydrolysed in the usual manner, the regenerated colouring matter being finally crystallised from dilute alcohol.

This new colouring matter, for which the name genistein is proposed, crystallises in long, glistening, colourless needles sparingly soluble in cold alcohol or acetic acid, and almost insoluble in water. An alcoholic solution gives, with basic lead acetate, a lemon-yellow precipitate, but with the neutral salt, except in large excess, only a slight separation is obtained. It is soluble in alkalis or in cold sulphuric acid, forming pale yellow solutions, and in cold nitric acid of sp. gr. 1.42, giving a dull brown coloration. With alcoholic potassium acetate, no potassium salt is produced, and with mineral acids in the presence of acetic acid, no acid compounds separate; the conclusion is therefore drawn that the hydroxyl groups in this compound are not present in relatively ortho-positions (this vol., 450). Alcoholic ferric chloride gives a dull reddish-violet coloration, which, on addition of excess of the reagent, becomes somewhat olive in tint. Genistein does not contain a methoxy-group.

Triacetylgenistein.—In the preparation of this derivative, the use of sodium acetate was not beneficial; the colouring matter was therefore digested with boiling acetic anhydride for 6 hours, the solution evaporated to a small bulk, alcohol added, and the crystalline separation collected and digested with a fresh quantity of the anhydride for 2 hours. The product, purified by crystallisation from alcohol, consisted of colourless needles melting at 197—201° and sparingly soluble in alcohol.

0.1145 gave 0.2622 CO_2 and 0.0448 H_2O . C = 62.45; H = 4.34. $C_{14}H_7O_5(C_2H_3O)_3$ requires C = 62.50; H = 4.17 per cent.

The acetyl groups were estimated by hydrolysing the compound with hydrochloric acid in the presence of boiling acetic acid, a method previously found serviceable in the analysis of tetracetylmorin (this vol., 448), and necessary owing to the tendency of the product to become sulphonated when sulphuric acid is employed.

0.5396 gave 0.3670 $C_{14}H_{10}O_5$. Found, 68.01. $C_{14}H_{7}O_5(C_{2}H_{3}O)_3$ requires $C_{14}H_{10}O_5 = 67.19$ per cent.

To obtain with some certainty a clue to the molecular weight of this colouring matter, its behaviour towards diasobenzene was studied, but the reddish-brown product was unfortunately of a resinous nature and not readily purified. Sufficient material was not available for further work in this direction, but if possible the reaction will be again investigated.

Tetrabromogenistein.—The colouring matter, made into a thin paste with acetic acid, was treated with bromine in excess; hydrogen bromide was at once evolved, and the mixture was allowed to stand for three days with frequent stirring. The product was drained on a porous tile, washed with boiling alcohol, crystallised first from a large volume of acetic acid, and finally from nitrobenzene. It forms a glistening mass of colourless needles melting above 290°, dissolves in dilute alkalis with a pale yellow colour, and is very sparingly soluble in boiling alcohol or acetic acid, but more readily in nitrobenzene. It does not dye mordanted calico.

0.1133 gave 0.1237 CO₂ and 0.0162 H₂O. C = 29.77; H = 1.58. $C_{14}H_6Br_4O_5$ requires C = 29.27; H = 1.04 per cent.

Decomposition Products of Genistein.

The substance was digested with boiling aqueous caustic potash of sp. gr. 1.46 for half an hour, or until the solution, which at first was yellow, had become brown, and on treatment with acid no longer gave a crystalline precipitate on cooling. The product, after neutralisation, was extracted with ether, the extract evaporated, the crystalline residue dissolved in water, and the solution saturated with sodium bicarbonate. Agitation with ether removed from this liquid a crystalline substance which after purification formed colourless needles melting at 210° and having the reactions of phloroglucinol. From the residual aqueous solution by acidification, and extraction with ether, a crystalline acid was isolated, which, after repeated crystallisation from water, formed long, thin, colourless leaflets melting at 147—149°.

0.0998 gave 0.2314 CO₂ and 0.0513 H₂O. C = 63.23; H = 5.71. $C_8H_8O_8$ requires C = 63.15; H = 5.26 per cent.

To ascertain its constitution, the acid was submitted to prolonged fusion with caustic potash at 240°. The product, isolated by solution in water, acidification, and extraction with ether, formed almost colour-

less needles melting at 208—210°, and was identified as parahydroxybenzoic acid. There is little doubt therefore that the acid melting at 147—149° was identical with Salkowski's parahydroxyphenylacetic acid (Ber., 1879, 12, 1438), obtained by the action of nitrous acid on paramidophenylacetic acid.

As was to be expected, the action of fused alkali at 240° on genistein gave phloroglucinol and parahydroxybenzoic acid.

Methylation of Genistein.

Genistein, dissolved in a solution of caustic potash (5 mols.) in methylic alcohol, was digested at the boiling point with excess of methylic iodide for three days. The product, after evaporation to a small bulk, became semi-solid, owing to the separation of crystals, which were collected by the aid of the pump, and washed first with a little dilute alcohol, and then with aqueous caustic potash. When crystallised from alcohol, the main bulk (D) melted at 137—139°, but a trace of a less soluble substance (E) melting at 187—189° was also present.

Analyses of D showed it to be genistein dinesthyl ether. It crystallised in colourless leaflets, melted at 137—139°, and was readily soluble in alcohol, but insoluble in aqueous solutions of alkalis.

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\begin{array}{lll} 0.1039 \; \text{gave} \; 0.2547 \; \text{CO}_2 \; \text{and} \; 0.0433 \; \text{H}_2\text{O}. & \text{C} = 66.85 \; ; \; \text{H} = 4.63. \\ 0.1472 \;\; \text{,,} & \text{by Zeisel's method,} \; 0.2560 \; \text{AgI.} & \text{CH}_3 = 10.52. \\ \text{C}_{14}\text{H}_8\text{O}_3(\text{OCH}_8)_2 \; \text{requires} \; \text{C} = 67.13 \; ; \; \text{H} = 4.89 \; ; \; \text{CH}_3 = 10.48 \; \; \text{per cent.} \end{array}
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An analysis of the regenerated genistein from the Zeisel determination gave the following numbers:

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0.1004 gave 0.2398 CO_2 and 0.0358 H_2O. C = 65.09; H = 3.96. C_{14}H_{10}O_5 requires C = 65.11; H = 3.87 per cent.
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As genistein contains three hydroxyl groups, it was evident that one had resisted methylation, and to confirm this point a small portion of the dimethyl ether was boiled with acetic anhydride and sodium acetate. The product crystallised from loohol in minute, colourless needles melting at 202—204°

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0.1140 gave 0.2773 CO_2 and 0.0485 H_2O. C = 66.33; H = 4.72. 0.1181 ,, 0.2855 CO_2 ,, 0.0520 H_2O. C = 65.93; H = 4.89. C_{14}H_7O_8(C_9H_9O)(OCH_9)_2 requires C = 65.86; H = 4.84 per cent.
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Sufficient material has not yet been available for an acetyl determination, but the compound was proved to be an acetyl derivative by hydrolysis in the usual manner; the regenerated product melted at 137—139°, and was identical with the dimethyl ether just described.

These reactions, whilst confirming the presence of three hydroxyl

groups in genistein, indicate that one of them is in the ortho-position relatively to a carbonyl group. An alcoholic solution of the ether, when treated with alcoholic potash, gives only a pale yellow liquid, and no insoluble potassium salt is precipitated.

The more insoluble substance, E, melting at 187—189° gave the following results on analysis:

0.1023 gave 0.2518 CO₂ and 0.0442 H₂O. C = 67.12; H = 4.80. 0.1537 ,, 0.2440 AgI. $CH_3 = 10.13$.

 $C_{14}H_8O_8(OCH_8)_2$ requires C = 67.13; H = 4.89; $CH_8 = 10.48$ per cent.

It is not dissolved by alkali solutions, and is apparently a second genistein dimethyl ether. As its melting point was very similar to that of the corresponding luteolin ether (Trans., 1896, 69, 211), and the contamination of the genistein employed with a trace of luteolin was possible, the regenerated colouring matter from the Zeisel determination was analysed, and proved apparently to be genistein.

0.0986 gave 0.2371 CO₂ and 0.0353 H₂O. C=65.57; H=3.97. $C_{14}H_{10}O_5$ requires C=65.11; H=3.87 per cent.

As the yield of this second ether was exceedingly small, amounting in all to not more than 0.5 gram, its further study has been impossible. It is conceivable that it is a dimethyl ether of a methylgenistein, a methyl group having entered the ring during methylation.

Dyeing Properties.

Although genistein is but a feeble dye-stuff, its tinctorial properties are important in connection with its constitution. The shades on mordanted woollen cloth resemble in general character those given by apigenin and vitexin.

	Chromium.	Aluminium.	Tin.	Iron.
Genistein.	vellow.	Very pale yellow.		
Vitexin.	yellow. Greenish-yellow.	Pale bright yellow.	Very pale yellow.	Pale brown, some- what dull.
Apigenin.	Yellow, with faint orange tint.	Pure yellow.	Not dyed.	Chocolate brown.

All these colouring matters yield parahydroxybenzoic acid on decomposition, and to the phenol nucleus which they contain must be due the power they have of producing chocolate brown shades with the iron mordant.

Theoretical Considerations.

The results of this investigation indicate that genistein contains three hydroxyl groups, one being in the ortho-position relatively to a carbonyl group, and that on decomposition it yields phloroglucinol and parahydroxyphenylacetic acid. Its dyeing properties, so closely resembling those of chrysin and apigenin, prove that it is not a simple ketone, for such a compound devoid of orthohydroxyl groups could not be a colouring matter. Most probably it is a trihydroxyphenylketocumaran.

the parent substance of which, ketocumaran, has been prepared and investigated by Friedlander and Neudörfer (Ber., 1897, 30, 1077). This constitution explains the formation of phloroglucinol and parahydroxyphenylacetic acid, and is in harmony with the results at present obtained. Various points of interest have yet to be studied before the formula is completely established; the work, however, can proceed but slowly, on account of the long operations involved in the preparation of pure genistein.

Dysing Properties of Genista tinctoria.—Experiments carried out in the usual manner indicated, as was to be expected, a close resemblance in this respect between dyer's broom and weld. The dyeing power of the former was distinctly the weaker of the two; otherwise, the only point of difference worthy of mention was that shown by the iron mordant, which, in the case of dyer's broom, gave a duller and more drab-coloured shade, and was evidently due to the genistein present.

II. HEATHER.

In former times, the common heath or heather, until recently named Erica vulgaris, was used as a dye-stuff, producing a yellow colour upon woollen goods (Crookes, Dyeing and Calico Printing, 1874, p. 511). Although now almost superseded, it was until recently employed in the home industries of outlying districts, such as the Highlands of Scotland. Bancroft (Philosophy of Permanent Colours, 1813, 2, 108) states that all five species of the erica or heather found in Great Britain are, he believes, capable of giving yellows much like those obtained with dyer's broom. According, however, to the experiments of J. J. Hummel (private communication), the Erica tetralia (bell-heather) and E. cinerea contain only traces of yellow colouring matter. Leuch refers to the tanning property of heather (Farben u. Farbekunds, 2, 320), and notes that the effect resembles in character that given by oak bark.

Experiment showed that the colouring matter was contained in the

green portion of the plant, and this alone was therefore employed for investigation. One colouring matter only was present, and this was extracted with boiling water, isolated by the method described for the preparation of luteolin from dyer's broom, and purified by crystallisation from dilute alcohol.

0.1245 gave 0.2721
$$CO_2$$
 and 0.0424 H_2O . $C=59.60$; $H=3.78$. $C_{15}H_{10}O_7$ requires $C=59.60$; $H=3.31$ per cent.

It formed a glistening mass of yellow needles, sparingly soluble in water, but somewhat readily so in alcohol. In alcoholic solution, ferric chloride caused a dark green coloration, and lead acetate gave an orange-yellow precipitate. The acetyl derivative, prepared in the usual manner, crystallised from alcohol in colourless needles melting at 191°.

0.1102 gave 0.2368
$$CO_2$$
 and 0.0381 H_2O . $C=58.60$; $H=3.84$. $C_{15}H_5O_7(C_2H_3O)_5$ requires $C=58.59$; $H=3.90$ per cent.

By fusion with alkali, two crystalline products were obtained, melting respectively at 210° and 195—196°; these consisted of phloroglucinol and protocatechnic acid. These results, together with comparative dyeing trials, prove that the colouring matter of the Calluna vulgaris is quercetin.

Dyeing Properties.

The dyeing properties of heather, although distinctly weaker, are so similar in character to those given by quercitron bark as to require no special description. Experiment showed that 36 parts of the heather were necessary to obtain as good a result as that given by 10 parts of quercitron bark.

Tanning Properties.—We are indebted to Prof. H. R. Procter for an analysis and examination of the tanning properties of heather:

Tanning matters absorbed by hide	6.4	per cent.
Soluble non-tanning matters	15.2	"
Insoluble at 60° F	70.4	"
Water	8.0	"
	100.0	

The leather, produced in the usual manner, although of a good colour, was very imperfectly tanned, and it appears that a large quantity of material and long tannage would be necessary for the production of a practically useful material. An infusion gives

a precipitate with bromine water and a green-black coloration with iron alum, reactions characteristic of a catechol tannin.

The investigation of dye-stuffs of a similar character will be undertaken as opportunity occurs.

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LXXX.—Researches on the Alkyl-substituted Succinic Acids. Part I. Methods of Preparation.

By WILLIAM A. Bone and Charles H. G. SPRANKLING.

THE alkyl-substituted succinic acids have a twofold interest to the organic chemist; firstly, because both individually and collectively they exhibit important stereochemical relationships concerning which much still remains to be cleared up, and, secondly, because certain members of the series are obtained as the result of the dry distillation. or oxidation, of important natural products or their immediate derivatives. They have thereby acquired quite a special significance in connection with discussions concerning the constitutions of these substances. Thus, unsymmetrical dimethylsuccinic acid is the chief oxidation product of Copaiba balsam (Levy and Engländer, Ber., 1885, 18. 3209), whilst trimethylsuccinic acid is formed both when camphoric acid is oxidised with chromic anhydride (Koenigs, Ber., 1893, 26, 2337) and when camphoronic acid is subjected to dry distillation (Helle, Inaug. Dies. Bonn, 1893; Bredt, Ber., 1893, 26, 3049). Although up to the present time some four or five general methods have been devised for the preparation of these acids, none of them can be considered as really satisfactory, because none of them enables us to conveniently obtain the acids in quantities sufficient for the thorough study of their properties, and more especially their stereochemical relations.

The methods which have so far been available for this purpose may be briefly reviewed in chronological order, as follows:

First Method.—This consists in preparing the nitriles of the acids by treating the dibromides of ethylene and its homologues in alcoholic solution with finely divided potassium cyanide. The nitriles are subsequently hydrolysed with concentrated hydrochloric acid.

Simpson (Annalen, 121, 164) in this way synthesised pyrotar-

taric (monomethylsuccinic) acid from propylene dibromide as long ago as 1863. Markownikoff repeated the synthesis in 1876 (Annalen, 182, 324), and, thirteen years later, Hell and Rothberg (Ber., 1889, 22, 1737) succeeded in preparing as-dimethylsuccinic acid from isobutylene dibromide, and were able to show that the synthetical acid was identical with that previously obtained by Levy and Engländer by the oxidation of Copaiba balsam (loc. cit.)

This method, theoretically important as it is, cannot be recommended for general use because of the very poor yields of the nitriles obtained. Thus, from 200 grams of propylene dibromide Markownikoff (loc. cit.) obtained under the most favourable conditions only 20 grams of the corresponding dicyanide. Again, in summarising their work on the action of potassium cyanide on isobutylene dibromide, Hell and Rothberg (loc. cit.) say: "Die Ausbeute an dem Nitril und damit an der Dimethylbernsteinsäure ist . . . eine sehr unbedeutende, und so fern empfiehlt sich die von uns angewandte Methode bis jetzt noch nicht zur Darstellung grösserer Mengen dieser Säure."

Second Method.—This was devised by Wislicenus in 1869 (Ber., 2, 720), and consists in preparing the diethylic salt of a symmetrically substituted alkylsuccinic acid by heating the ethylic salt of an a-bromofatty acid with finely divided silver. The following general equation, in which R stands for an alkyl radicle, represents the reaction which is supposed to occur:

$$2R \cdot CHBr \cdot COOEt + 2Ag = \frac{R \cdot CH \cdot COOEt}{R \cdot CH \cdot COOEt} + 2AgBr.$$

Wislicenus employed the method for the preparation of "dimethylsuccinic acid "from ethylic a-bromopropionate. The syrupy acid which he obtained on hydrolysis of the resulting ethereal salt could hardly be a s-dimethylsuccinic acid, since both of these crystallise exceedingly well, and melt at 127° and 209° respectively. Hell and Wittekind (Ber., 1874, 7, 319), by the action of silver on ethylic a-bromisobutyrate and subsequent hydrolysis of the resulting ethylic salt, obtained an acid melting at 95° which they described as tetramethylsuccinic acid, but which was shown by V. Meyer and Auwers (Ber., 1889, 22, 3005; 1890, 23, 295) to be in reality aga,-trimethylglutaric acid. These investigators were able to prove that the reactions which occur when the ethylic salt of an a-bromo-substituted fatty acid is heated with molecular silver are in reality very complex. A part of the a-bromo-ethereal salt reacts normally with the silver, according to the equation just given. Another part is converted into the β -bromoethereal salt by the elimination of, and subsequent recombination with, hydrogen bromide, and this β -bromo-ethereal salt reacts with the silver and the a-bromo-ethereal salt in a manner expressed by such equations as the following:

Thus, from ethylic a-bromisobutyrate they obtained a 15 per cent. yield of a mixture of about equal quantities of aaa_1 -trimethylglutaric acid (m. p. 95°) and tetramethylsuccinic acid (m. p. 147°).

This method, partly on account of the complications indicated, and partly also on account of the very poor yields obtained by it, cannot be recommended except for the preparation of tetra-alkyl-substituted succinic acids, in which cases it is the only one at present available.

Third Method.—In 1878—1879, Conrad and others (Conrad, Annalen, 188, 217; Kressner, ibid., 192, 135; Hardtmuth, ibid., 192, 142; Huggenberg, ibid., 192, 146; Conrad and Limpach, ibid., 192, 153) showed that ethylic sodioacetoacetate reacts very readily in alcoholic solution with ethylic bromacetate (or a-bromopropionate) giving a 65 per cent. yield of ethylic acetosuccinate (or β -methylacetosuccinate), according to the equation:

$$\begin{array}{c} \mathrm{CH_8 \cdot CO \cdot CHNa} \\ \mathrm{COOEt} \end{array} + \begin{array}{c} \mathrm{Br \cdot CH_2} \\ \mathrm{COOEt} \end{array} = \begin{array}{c} \mathrm{CH_8 \cdot CO \cdot CH - - - CH_2} \\ \mathrm{COOEt} \end{array} + \mathrm{NaBr}.$$

Both ethylic acetosuccinate and β -methylacetosuccinate contain a hydrogen atom in the α -position replaceable by alkyl radicles. Kressner (loc. cit.), on methylating ethylic acetosuccinate, obtained 30 per cent. of the theoretical yield of ethylic α -methylacetosuccinate, and Hardtmuth (loc. cit.) succeeded in preparing $\alpha\beta$ -dimethylacetosuccinate by methylating the β -methylacetosuccinate.

Since these ethylic acetosuccinates on hydrolysis with alcoholic potash or dilute mineral acids gave about 75 per cent. of the theoretical yields of the corresponding succinic acids, it seemed probable that any mono-, di-, or tri-alkylsuccinic acid could be readily prepared in quantity from ethylic acetoacetate.

Unfortunately, further investigation seemed to show that, whilst this reaction served very well for the preparation of succinic acid or its monalkyl derivatives, in other cases it was unsatisfactory. Hardtmuth (loc. cit.), for example, described as s-dimethylsuccinic acid a substance melting at 165—167° obtained by this method. This could hardly be either of the s-dimethylsuccinic acids, which melt at 127° and 209° respectively, although our own experience leads us to think that it probably contained both of them in an impure condi-

tion. Further, Barnstein (Annalen, 1887, 242, 126), on attempting to prepare as-dimethylsuccinic acid from the product of the interaction of ethylic α -bromisobutyrate and ethylic sodioacetoacetate in alcoholic solution, found that, owing to a series of complex reactions it was impossible to isolate even a small quantity of a homogeneous product from the resulting mixture of ethereal salts.

We have thoroughly reinvestigated this method, paying particular attention to the yields and also to the degree of purity of the acid obtained in each case. Our experiments do not altogether bear out the statements made in the preceding paragraphs. It is quite true that the yield of the succinic acid shows a marked falling off in the cases of the di- and tri-substituted members of the series. This seems to be due to two causes: (1) The fact that the yield of the acetosuccinate is considerably less when ethylic a-bromisobutyrate is condensed with ethylic sodioacetoacetate, or its methyl derivative, than in similar experiments in which ethylic bromacetate or a-bromopropionate is employed; (2) the quantity of the succinic acid obtained by the hydrolysis of a methyl-substituted ethylic acetosuccinate appears to diminish with the number of methyl groups present; at the same time, the ketonic hydrolysis occurs to a greater extent in such cases, and it is more difficult to obtain the acid in a pure condition. We are, however, quite unable to confirm Barnstein's statement (loc. cit.), as in all cases we were able to isolate a very fair quantity of the acetosuccinate in a tolerably pure condition, but the method compares unfavourably with those we shall discuss later.

Fourth Method.—In 1882, Bischoff (Annalen, 214, 38) showed that the preceding method could be improved upon by substituting ethylic malonate, or one of its alkyl derivatives, for ethylic aceto-acetate. He found, for example, that ethylic sodiomalonate, in the presence of alcohol, readily reacts with ethylic bromacetate or a-bromopropionate, forming the ethereal salt of a tricarboxylic acid, which, when hydrolysed and heated at 200° until all evolution of carbonic anhydride had ceased, yielded a succinic acid. The reactions involved, it was supposed, could be represented by such equations as the following:

$$(1) \ CH_{s} \cdot CHB_{t} \cdot COOEt + NaCH < \begin{array}{c} COOEt \\ COOEt \end{array} = \begin{array}{c} CH_{s} \cdot CH \cdot COOEt \\ COOEt + NaBr, \\ COOEt \end{array}$$

(2)
$$CH_3 \cdot CH \cdot COOEt$$

 $CH < COOEt + 3H_2O = CH_3 \cdot CH \cdot COOH + 3C_2H_5OH + CO_2.$

The quantity of the succinic acid finally obtained was, as a rule, about 30 per cent. of that theoretically possible from the amount of ethylic malonate, or its methyl derivative, originally used.

Quite a number of syntheses of alkyl-substituted succinic acids were effected by this method during the next few years, among which the following were of special interest.

Propyl- and isopropyl-succinic acids (Waltz, Annalen, 1882, 214, 58; Roser, ibid., 1883, 220, 271).

s-Dimethylsuccinic acids (Bischoff and Rach, Annalon, 1886, 234, 54; Leuckart, Bor., 1885, 18, 2344).

as-Dimethylsuccinic acid (Barnstein, Annalen, 1887, 242, 126; Leuckart, loc. oit.).

In 1890, Bischoff and Mintz (Bor., 23, 647), described as "trimethylsuccinic acid" an acid melting at 105° which they had prepared from the product of the action of ethylic a-bromisobutyrate on an alcoholic solution of ethylic sodiomethylmalonate. was, however, shown by Auwers and Jackson (Ber., 1890, 23, 1599) to be identical with the aa₁-dimethylglutaric acid melting at 102—104° prepared by Zelinsky in 1889 from the product of the interaction of methylene iodide and the sodium compound of ethylic a-cyanopropionate (Ber., 1888, 22, 2823). A long discussion ensued as to the nature of the acid, but it was finally admitted on all sides that it was an aa₁-dimethylglutaric acid.* In order to explain its formation from ethylic sodiomethylmalonate and ethylic a-bromisobutyrate, Auwers supposed that the latter, under the conditions of the experiment, loses hydrogen bromide, forming ethylic methacrylate, and that this then condenses with the ethylic methylmalonate, forming the ethylic salt of a tricarboxylic acid, which on subsequent treatment would yield aa1-dimethylglutaric acid.† The reactions involved would therefore be somewhat as follows:

^{*} The acid in question, it may be stated, was afterwards shown to be a mixture of cis- and trans-aa₁-dimethylglutaric acids in molecular proportion (Auwers and Thorpe, Ber., 1895, 28, 623; Annalen, 1895, 285, 310; Bone and Perkin, Trans., 1896, 69, 268).

[†] It should also be recorded that, twenty years ago, Tate (Inaug. Diss. Wursburg) described as "as-dimethylsuccinic acid" an acid melting at 76° which he obtained from the product of the interaction of ethylic sodiomalonate and ethylic

We have thoroughly studied the interactions of ethylic sodiomalonate and its methyl derivative in alcoholic solution with ethylic a-bromopropionate and a-bromisobutyrate respectively. In all cases, we find that the a-bromethylic salt in part loses hydrogen bromide, forming an unsaturated ethylic salt which then condenses with the ethylic malonate (or methylmalonate), so that the product is a mixture of isomeric ethylic tricarboxylates which cannot be separated by fractional distillation. On hydrolysis with concentrated hydrochloric acid, the oil yields a mixture of isomeric succinic and glutaric acids. In one case, namely, that of ethylic sodiomethylmalonate and ethylic a-bromisobutyrate, nothing but aa,-dimethylglutaric acid is finally obtained; in other cases, the ratio between the succinic and glutaric acid in the final product lies between 2:1 and 4:5:1; this ratio appears to remain unchanged when the mixture of ethylic tricarboxylates obtained in the first reaction is methylated before being hydrolysed. This part of our work will be more fully discussed later. In order to separate the succinic acid from the isomeric glutaric acid in the final product, one of two methods may be adopted. The mixture of ethylic tricarboxylates may be hydrolysed with 50 per cent. sulphuric acid, whereby the tricarboxylic acids lose carbonic anhydride as soon as they are formed, yielding a mixture of isomeric succinic and glutaric acids. The succinic acid is then immediately converted into its anhydride, and this being volatile, may be separated from the glutaric acid by steam distillation (Auwers, Annalen, 1895, 285, 217). Our own experience goes to show that this plan is not altogether satisfactory, the separation so effected being at best incomplete, and we have abandoned it for another based on the fact that the calcium salts of alkyl-substituted succinic acids are very sparingly soluble in water, whilst those of the isomeric glutaric acids are quite soluble. The details of this method will be fully explained later on in this paper.

Fifth Method.—This was devised by Zelinsky (Ber., 1891, 24, 489) for the preparation of trimethylsuccinic acid. It has already been explained that this acid cannot be prepared from the product of the interaction of ethylic sodiomethylmalonate and ethylic a-bromiso-butyrate in alcoholic solution. If, however, the sodium compound of ethylic a-cyanopropionate be substituted for the ethylic sodiomalonate, a certain amount of trimethylsuccinic acid is obtained. This method

α-bromisobutyrate. This acid has been frequently described as such in chemical literature, but it is in reality α-monomethylglutaric acid (m. p. 76°); as-dimethyl-succinic acid melts at 140°.

^{*} The authors will show later, however, that trimethylsuccinic acid may be obtained in fairly large quantities by methylating the product of the interaction of ethylic sodiomalonate and ethylic a-bromisobutyrate, and subsequently hydrolysing he methylated oil.

was employed by one of us, in conjunction with Professor W. H. Perkin (Trans., 1895, 67, 416), and is fully described in that paper. It was then shown that the product of the interaction of the sodium compound of ethylic a-cyanopropionate and ethylic a-bromiso-butyrate consists of a mixture of ethylic trimethylcyanosuccinate and aa_1 -dimethylcyanoglutarate, owing to the fact that some of the a-bromisobutyrate, under the conditions of the experiment, loses hydrogen bromide, forming ethylic methacrylate, which then condenses with the ethylic a-cyanopropionate in the following manner:

$$\mathbf{CH_3 \cdot CH(CN) \cdot COOEt} + \frac{\mathbf{CH_2}}{\mathbf{CH_3}} \mathbf{>} \mathbf{C \cdot COOEt} = \frac{\mathbf{CH_3 \cdot C(CN) \cdot CH_2 \cdot CH \cdot CH_3}}{\mathbf{COOEt}}$$

The product, therefore, on hydrolysis with concentrated hydrochloric acid, yielded a mixture of trimethylsuccinic and aa_1 -dimethylglutaric acids, in which the latter predominated.

We have made many experiments with the object of improving the yield of trimethylsuccinic acid by this method, without meeting with any great measure of success. [At best, the ratio of trimethylsuccinic to aa₁-dimethylglutaric acid finally obtained does not amount to more than 1:2, and we have been compelled to abandon the method alto-Incidentally, it may be remarked that Auwers, in an account of this method (Annalen, 1895, 285, 247), states that he obtained a much better yield of trimethylsuccinic acid in experiments in which ethylic a-cyanopropionate, prepared by the action of potassium cyanide on ethylic a-bromopropionate, was employed than in those where the a-cyanopropionate used had been prepared by the methylation of ethylic We have carefully investigated this point, and are cyanacetate. unable to confirm his statement. Our experience goes to show that the final result is in no way affected by the manner in which the ethylic a-cymnopropionate employed is obtained.

New Method.—More than a year ago, one of us was led to investigate ethylic cyanacetate as a possible starting-point for the preparation of succinic acids. It has already been explained that the ethylic salts of a-bromo-fatty acids exhibit a tendency, in the presence of alkaline liquids such as an alcoholic solution of ethylic sodiomalonate, to lose hydrogen bromide forming the ethylic salts of unsaturated acids. Hence it is impossible to prepare an alkyl-substituted succinic acid from ethylic malonate, or its methyl derivative, without at the same time producing a considerable quantity of an isomeric glutaric acid.

Now when ethylic cyanacetate is added to an alcoholic solution of sodium ethylate, its sodium derivative, being practically insoluble in alcohol, at once separates as a finely divided white solid. If this is quickly removed by filtration, the alcoholic filtrate has an almost neutral reaction. It seemed probable, therefore, that if the ethylic salt

of an a-bromo-fatty acid were digested with the sodium compound of ethylic cyanacetate suspended in alcohol, the tendency of the bromo-ethereal salt to lose hydrogen bromide would not come into play. In such a case the interaction would proceed normally, to the exclusion of secondary changes due to the tendency referred to, and the product would be an ethylic cyanosuccinate, as indicated by such equations as the following, where R represents an alkyl radicle:

$$\begin{array}{c} \text{CN} \\ \text{COOEt} \\ \text{COOEt} \\ \text{CHNa} + \text{R} \cdot \text{CHBr} \cdot \text{COOEt} = \\ \\ \text{COOEt} \\ \text{CHNa} + \text{R} \\ \text{COOEt} \\ \text{COOEt} \\ \text{CHNa} + \text{R} \\ \text{COOEt} $

This proved to be the case. The sodium compound of ethylic cyanacetate reacts very readily with the ethylic salts of a-bromo-fatty acids, and the yields of the pure substituted ethylic cyanosuccinates amount to approximately 60 per cent. of the theoretical. Further, since these contain a hydrogen atom replaceable by sodium, indicated by an asterisk in the formulæ given above, they may be easily alkylated. The yields of alkylated products vary between 70 and 90 per cent. of the theoretical in different cases.

Thus it is possible to prepare in quantity any mono-, di-, or tri-alkyl-substituted ethylic cyanosuccinate in a state of purity. These are very readily hydrolysed by means of concentrated hydrochloric acid, and the yields of the corresponding succinic acids amount to 80 per cent. of those theoretically obtainable according to the equation:

$$\begin{array}{c} \text{CN} \\ \text{COOEt} \\ \end{array} \\ \text{CH} \cdot \text{C} \\ \begin{array}{c} \text{R} \\ \text{COOEt} \\ \end{array} \\ + \text{HCl} + 4\text{H}_2\text{O} = \\ \\ \text{COOH} \cdot \text{CH}_2 \cdot \text{C} \\ \begin{array}{c} \text{R} \\ \text{COOH} \\ \end{array} \\ + \text{NH}_4\text{Cl} + 2\text{C}_2\text{H}_5 \cdot \text{OH} + \text{CO}_2. \end{array}$$

A very careful examination of the products of hydrolysis has shown that in no case is a glutaric acid present.

We have prepared the ethylic salts of monomethyl-, s-dimethyl-, as-dimethyl-, and trimethyl-cyanosuccinic acids, and have carefully studied their physical properties. From them we have obtained the corresponding succinic acids in considerable quantities, and have been able to investigate more thoroughly than heretofore their anhydrides, anilic acids, and highly characteristic calcium salts; finally, we

have determined the dissociation constants of the whole series. The results of these experiments are given in the present paper.

We have also prepared s-dipropyl- and s-di-isopropyl-succinic acids by the new method, and hope to publish an account of their properties at an early date.

EXPERIMENTAL.

A. Preparation of Substituted Succinic Acids from Ethylic Acetoacetate.

The object of this part of our work was to determine the quantities of methyl-substituted succinic acids obtainable by Conrad's method from ethylic acetoacetate (see p. 841). Our experiments may be conveniently divided into two series; (1) those bearing upon the interaction of ethylic sodioacetoacetate, or its methyl derivative, and ethylic α-bromopropionate or α-bromisobutyrate; (2) those dealing with the methylation of the resulting ethylic acetosuccinates.

First Series.—The method adopted in each experiment was as follows: To the solution of 5.75 grams of sodium in 70 grams of ethylic alcohol were added a quarter of a gram-molecule of ethylic acetoacetate, or its methyl derivative, and rather more than the calculated quantity of the α-bromo-ethereal salt. The whole was heated on the water-bath in a reflux apparatus until the liquid had become neutral. Thereupon the greater part of the alcohol was distilled off and the residue poured into water. The oil which separated was extracted with ether in the usual manner. After drying the ethereal solution over calcium chloride and distilling off the ether, the residual oil was carefully fractionated at a pressure of about 35 mm. The yield of acetosuccinate was then noted, and its purity tested by analysis.*

The acetosuccinate was thereupon hydrolysed by boiling it with alcoholic potash in a reflux apparatus. The alcohol was then removed by evaporation on the water-bath, and after the residue had been dissolved in water, an excess of hydrochloric acid was added. The solution was finally saturated with ammonium sulphate, thoroughly extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate. After distilling off the ether, the residue was dissolved in water, and the solution made alkaline with ammonia. The liquid was filtered and the filtrate boiled with excess of a 25 per cent. solution of calcium chloride. The insoluble calcium salt of the substituted succinic acid which was at once precipitated was collected by the aid

^{*} We have not considered it necessary to include these analyses in the paper; we may say, however, that they indicated that the acetosuccinate was in each case tolerably pure.

of the pump, quickly washed with water, dried at 100°, and weighed. The amount of acid corresponding to it was then calculated, allowance being made in each case for the water of crystallisation in the salt, which is not expelled at a temperature below 120°. The calcium salt was finally decomposed by dissolving it in hot concentrated hydrochloric acid, and the acid which separated on cooling was carefully examined. In each case, it proved to be a substituted succinic acid.

The results of these experiments may be tabulated as follows:

TABLE I.

Interaction.	Time required for completion of interaction.	Percentage yield of acetosuccinste.	B. p. of acetosuccinate under 25 num. pressure.	Percentage yield of succinic acid.	M. p. of succinic acid.
Ethylic acetoacetate and ethylic a-bromopropionate	16 hrs.	70	155—157°	42	{ 109—111° (monomethyl)
Ethylic acetoacetate and ethylic a-bromisobutyrate	4 days	44	160—170°	18	(140—141° ((as-dimethyl) (205°
$\begin{array}{c} Ethylic methylace to accetate and \\ ethylic \alpha\text{-bromopropionate} \end{array} \right)$	17 hrs.	52	155—162°	26	(trans-s-dimethyl) 126—127°
Ethylic methylacetoacetate and ethylic α -bromisobutyrate	2½ days	18	167—174°	5	(cis-s-dimethyl) 146—148° (trimethyl)

^{*} N.B.—Figures in this column express the percentage yield of the succinic acid obtained in each case in terms of that theoretically possible from the amount of the acetoacetate originally taken in the experiment.

Second Series.—Ethylic acetosuccinate, and its β -methyl and $\beta\beta$ -dimethyl derivatives, contain a hydrogen atom in the α -position replaceable by alkyl groups. Their sodium compounds were accordingly treated with methylic iodide in alcoholic solution, and the methylated products isolated and fractionated under diminished pressure in a manner similar to that already described. After noting the yield, which in each case amounted to about 80 per cent. of the theoretical, the oil was hydrolysed with alcoholic potash, and the resulting succinic acids were finally obtained and estimated as calcium salts. The results of these experiments are tabulated on p. 849, the yields of succinic acids for purposes of comparison being stated in terms of the amounts theoretically obtainable from the quantity of ethylic aceto-acetate originally employed for the preparation of the acetosuccinate (compare Table I).

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Ethylic salt methylated.	Percentage yield of methylated product.	B. p. of product under 30 mm. pressure.	Percentage yield of succinic acid.	M. p. of succinic acid.
Ethylic acetosuccinate.	82.5	170—175°	14	112° (monomethyl)
Ethylic β-methyl- acetosuccinate	80.0	160—162°	26	128—129 ⁸ (cis-s-dimethyl)
Ethylic &&-dimethyl- acetosuccinate	81.0	175—182°	10.5	147—148° (trimethyl)

B. Preparation of Substituted Succinic Acids from Ethylic Malonate: Separation of Isomeric Methyl-substituted Succinic and Glutaric Acids.

The object of these experiments was to determine the actual quantities of isomeric succinic and glutaric acids obtainable as the result of the interaction of ethylic sodiomalonate, or its methyl derivative, and ethylic a-bromopropionate, or a-bromisobutyrate, and subsequent hydrolysis of the resulting mixture of ethylic tricarboxylates with concentrated hydrochloric acid (see p. 842). The method employed in each case was identical with that given under section A, except in so far as ethylic malonate, or its methyl derivative, was used instead of ethylic acetoacetate. The product was isolated and fractionated under reduced pressure in much the same manner as there described (p. 847). The resulting mixture of ethylic tricarboxylates was hydrolysed by boiling it in a reflux apparatus on a sand-bath with excess of concentrated hydrochloric acid until the whole of the oil had disappeared. In some cases, part of the succinic acid separated on cooling; if so, it was at once removed by filtration at the pump, dried on porous plates, and then at 100°. The filtrate, or the original liquid, in cases where no acid separated, was made alkaline with strong ammonia, and the solution of ammonium salts boiled with excess of a 25 per cent. solution of calcium chloride, whereby the insoluble calcium salt of the succinic acid present was at once precipitated. This was collected by the aid of the pump, washed with water, dried at 100° and weighed. The quantity of acid corresponding to it was then calculated, allowance being made in each case for the water of crystallisation in the salt which is not expelled below 120°. The calcium salt was afterwards decomposed by dissolving it in hot concentrated hydrochloric acid, and the acid which separated out on cooling examined. In each case, it proved to be a succinic acid. To the filtrate from the insoluble calcium salt was added an excess of strong hydrochloric Digitized by \$300gle

acid, it was then saturated with ammonium sulphate, thoroughly extracted with ether, and the ethereal solution dried over anhydrous sodium sulphate. After distilling off the ether, an acid oil, which crystallised on standing in a vacuum over sulphuric acid, always remained. The residue was in each case recrystallised from a mixture of benzene and light petroleum, and the recrystallised acid examined; it always proved to be a glutaric acid isomeric with the succinic acid obtained from the insoluble calcium salt.

The results of these experiments are given in Table III, which shows the yields of isomeric succinic and glutaric acids respectively obtained in each case, in terms of the amounts theoretically possible from the quantity of ethylic malonate or methylmalonate used.

Percentage Melting points. vield. Ratio. ethylic i oxylates Interaction. Succinic acid. Succinic: glutaric. Succinic. Glutaric. Ethylic malonate and ethylic a-75 bromopropionate 58 12.5 4.5:1 110---111° 96-98° Ethylic malonate and othylic abromisobutyrate. 77 44 22 2:1 141--142° 76° methyl-Ethylic malonate ethylic a-bromo-208° propionate 61 89 10 4:1 123-124° Ethylic methylmalonate and ethylic a-bromisobutyrate..... 61 nil 50 101-103°* all glutaric

TABLE III.

One very curious feature in connection with these experiments is the fact that whilst ethylic a-bromisobutyrate reacts with ethylic sodiomalonate giving a mixture of ethylic tricarboxylates which on hydrolysis with concentrated hydrochloric acid yield a considerable quantity of as-dimethylsuccinic acid, no trimethylsuccinic acid can be obtained under similar conditions from the product of the interaction of ethylic a-bromisobutyrate and ethylic sodiomethylmalonate. We have many times tried the experiment, but always with the same result, and our experience is confirmed by that of other workers.

^{*} Mixture of cis- and trans-aa1-dimethylglutaric acids.

It is evident that the product of the interaction of ethylic sodio-malonate and ethylic a-bromisobutyrate must consist of a mixture of the ethylic tricarboxylates, $(COOEt)_2CH\cdot C(CH_3)_2\cdot COOEt$ and $(COOEt)_2CH\cdot CH_2\cdot CH(CH_3)\cdot COOEt$, in which the first greatly predominates, for the ratio between the as-dimethylsuccinic and a-methylglutaric acids obtained on hydrolysing the product with strong hydrochloric acid is 2:1. Both these tricarboxylates contain a hydrogen atom in the a-position replaceable by alkyl radicles. The methylated product on hydrolysis should, therefore, give a considerable amount of trimethylsuccinic acid, and this proved to be the case. The following are the details of the experiment.

To the solution of 3.35 grams of sodium in 40 grams of ethylic alcohol were added 40 grams of the refractionated product of the interaction of ethylic sodiomalonate and α-bromisobutyrate (b. p. 155—163° under 18 mm. pressure); no solid sodium derivative separated out. 25 grams of methylic iodide were then very carefully added, for much heat was evolved. The liquid was heated for 1½ hours on the water-bath until it became quite neutral. It was then poured into water, and the oil extracted with ether; the ethereal solution, after washing with a dilute solution of sodium thiosulphate, was dried over calcium chloride, and after distilling off the ether, the residual oil was fractionated under 20 mm. pressure. A fraction amounting to 32 grams distilled over at 164—166°, the yield being 76 per cent, of that theoretically obtainable.

The whole was now hydrolysed by boiling it with excess of concentrated hydrochloric acid in a reflux apparatus for 5 hours. No acid separated out on cooling. The trimethylsuccinic and aa_1 -dimethylglutaric acids were then separated by means of their calcium salts in a manner similar to that already described, and we finally obtained 11 grams of trimethylsuccinic acid (m. p. $145-147^{\circ}$) and 5.2 grams of a mixture of cis- and trans- aa_1 -dimethylglutaric acids (m. p. $102-105^{\circ}$). The total yield of acid was 16.2 grams or 90 per cent. of that theoretically possible from the quantity of oil hydrolysed, and the ratio between the trimethylsuccinic and aa_1 -dimethylglutaric acids was 2:1. From the results recorded in Table III, together with those of the experiment just described, it will be seen that 35 per cent. of the theoretical yield of trimethylsuccinic acid may be obtained from ethylic malonate.

C. Preparation of Trimethylsuccinic Acid from Ethylic a-Cyanopropionate.

It has already been stated that a mixture of trimethylsuccinic and aa₁-dimethylglutaric acids is obtained when the product of the inter-

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action of the sodium compound of ethylic a-cyanopropionate and ethylic a-bromisobutyrate is hydrolysed with concentrated hydrochloric acid (p. 845). Up to the present time, this has been the only method by which trimethylsuccinic acid has been prepared synthetically in any quantity. We have made a large number of experiments with this method, which is carried out in exactly the same way as that already given for the preparation of succinic acids from ethylic malonate (section B), except, of course, that the latter is replaced by a molecular proportion of ethylic a-cyanopropionate. The resulting mixture of ethylic trimethylcyanosuccinate and aa_1 -dimethylcyanoglutarate was hydrolysed by means of concentrated hydrochloric acid, and the trimethylsuccinic and aa_1 -dimethylglutaric acids separated by means of their calcium salts as described in the preceding section.

The ethylic a-cyanopropionate used in the first series of experiments was prepared by the action of potassium cyanide on an alcoholic solution of ethylic a-bromopropionate (Bone and Perkin, Trans., 1895, 67, 421), whilst in the second series, ethylic a-cyanopropionate prepared by the methylation of ethylic cyanacetate was employed. Our results may be tabulated as follows:

TABLE IV.

_	Percentage yield of mixture of cyanosuccinate and cyanogutarate.	Percentage yield of tri- methylsuccinic acid.	Percentage yield of ea ₁ -di- methylglutaric acids.	Ratio. Succinic: glutaric.
1st series	I	15	25	3:5
2nd ,,		15	80	1:2

D. Preparation of Ethylic Methylcyanosuccinates from Ethylic Cyanacetate.

The sodium compound of ethylic cyanacetate readily reacts with ethylic a-bromopropionate or a-bromisobutyrate, yielding a substituted ethylic cyanosuccinate as already explained (p. 845). The ethylic β -monomethyl- and $\beta\beta$ -dimethyl-cyanosuccinates so produced each contain a replaceable hydrogen atom, and on methylation therefore yield ethylic $\alpha\beta$ -dimethyl- and trimethyl-cyanosuccinates respectively. It is thus possible to prepare any methyl-substituted ethylic cyanosuccinate from ethylic cyanacetate, and these reactions afford a new method for the preparation of the corresponding succinic acids.

(1) Ethylic β -Methylcyanosuccinate, $\frac{\text{CN}}{\text{COOEt}}$ \sim CH \sim C

-28.5 grams of ethylic cyanacetate were added to a solution of 5.75 grams of sodium in 70 grams of absolute alcohol and to the thick paste of the white insoluble sodium compound so formed, 42 grams of ethylic a-bromopropionate were very carefully added. The sodium compound immediately dissolved with great evolution of heat, and a moment later sodium bromide separated out. After heating on the water-bath for an hour, the liquid became quite neutral. It was thereupon cooled, poured into water, and the oil which separated was extracted with ether; the ethereal solution was washed, first with dilute sodium carbonate, then with water, and finally dried over calcium chloride. On distilling off the ether, a yellowish oil remained, which was carefully fractionated under 24 mm. pressure. A small quantity of liquid, consisting of a mixture of unchanged ethylic cyanacetate and a-bromopropionate, passed over between 80° and 140°, the temperature rising rapidly the whole time; the greater part of the product distilled over between 140° and 165°, and a very small quantity of an oil of higher boiling point remained behind in the apparatus. The last fraction is now being investigated.

The main product was refractionated under a pressure of 17 mm., and the portion distilling over at 160—165° was collected separately. On analysis, it gave the following numbers:

From four such preparations the total quantity of refractionated oil obtained was 150 grams, or 70 per cent. of the theoretical yield.

(2) Methylation of Ethylic β-Methylcyanosuccinate. Ethylic aβ-Dimethylcyanosuccinate.—53·5 grams of ethylic β-methylcyanosuccinate were added to a solution of 5·75 grams of sodium in 70 grams of ethylic alcohol; the liquid became warm, but no solid sodium compound separated out. The contents of the flask were well cooled, and rather more than the calculated quantity of methylic iodide was very carefully added in five or six portions. As soon as the first portion had been added, a very vigorous reaction began, so much heat being evolved that the liquid began to boil, and it was necessary to attach the flask to a long Allihn's condenser in order to avoid loss of the iodide. Half an hour's heating on the water-bath after the addition of the last portion of the iodide sufficed to complete the process. The liquid was then poured into water, and the oil which separated was extracted with ether. The ethereal solution was washed with a dilute solution of sodium thiosulphate, then with aqueous sodium carbonate, finally

with water, and after being dried over calcium chloride, the ether was distilled off. The greater part of the residual oil distilled between 155° and 165° under 15—20 mm. pressure; this was refractionated at the same pressure, when it passed over between 159° and 162°. The refractionated oil was analysed, with the following results:

```
0.2038 gave 0.4352 CO<sub>2</sub> and 0.1405 H_2O. C = 58.24; H = 7.66. 0.2000 , 0.4242 CO<sub>2</sub> , 0.1361 H_2O. C = 57.84; H = 7.56. 0.1932 , 10.2 c.c. nitrogen at 8° and 770 mm. N = 6.46. C_{11}H_{17}O_4N requires C = 58.14; H = 7.48; N = 6.16 per cent.
```

The yield was 75 per cent. of that theoretically possible.

(3) Ethylic $\beta\beta$ -Dimethylcyanosuccinate.—Ethylic a-bromisobutyrate acts much less vigorously than ethylic a-bromopropionate on ethylic sodiocyanacetate. Experiments in which the reaction was carried out under the same conditions as those described for the preparation of ethylic β -methylcyanosuccinate did not give good results. The alcoholic liquid became neutral only after some 18 to 24 hours heating on the water-bath, and the yield of the $\beta\beta$ -dimethylcyanosuccinate was by no means satisfactory, a considerable quantity of an oil of higher boiling point being produced.

A much better result was obtained by adding 28.5 grams of ethylic cvanacetate to a solution of 5.75 grams of sodium in 70 grams of ethylic alcohol contained in a soda-water bottle. The sodium compound separated as a thick white paste. Rather more than the calculated quantity of ethylic a-bromisobutyrate was then added, and the bottle, securely corked, was heated at 100° in a water-bath for 6 hours. Five or six such bottles were usually heated at once, and the products afterwards worked up together in the manner to be described. The liquid, which acquired a deep magenta colour and became quite neutral during the process, was poured into water and acidified with dilute hydrochloric acid. The dark red oil which separated was extracted with ether; the ethereal solution had a deep magenta colour, but this was entirely removed after repeatedly washing it with dilute sodium carbonate solution and with water. The ethereal solution was then dried over calcium chloride, the ether distilled off, and the yellow oil which remained was fractionated under a pressure of 10 mm. A fair quantity of a mixture of unchanged ethylic cyanacetate and a-bromisobutyrate passed over between 80° and 145°, but the greater part of the oil distilled between 145° and 165°, leaving a very small residue of an oil of higher boiling point in the distillation flask.

The main product was refractionated under a pressure of 15 mm., and the portion passing over at 166—170° collected separately; this was analysed, with the following results:

0.1612 gave 0.3446 CO_2 and 0.1129 H_2O . C = 58.05; H = 7.78. 0.1479 ,, 0.3141 CO_2 ,, 0.1000 H_2O . C = 57.90; H = 7.51. 0.1857 ,, 9.4 c.c. nitrogen at 6° and 772 mm. N = 6.27. $C_1H_{12}O_2N$ requires C = 58.14; H = 7.48; N = 6.16 per cent.

From thirteen such preparations, 428 grams of the refractionated product were obtained, the yield being 58 per cent. of the amount theoretically possible.

(4) Methylation of Ethylic $\beta\beta$ -Dimethylcyanosuccinate. Ethylic Trimethylcyanosuccinate.—This operation was carried out in exactly the same way as that given for the methylation of ethylic methylcyanosuccinate, so that it is not necessary to describe it in detail. The reaction between the methylic iodide and the sodium derivative of the cyanosuccinate was again very vigorous, and the yield of refractionated product was 90 per cent. of that theoretically obtainable. On analysing the oil, the following results were obtained:

```
0·1700 gave 0·3702 CO<sub>2</sub> and 0·1220 H<sub>2</sub>O. C=59·36; H=7·97. 0·1416 ,, 0·3090 CO<sub>2</sub> ,, 0·1023 H<sub>2</sub>O. C=59·53; H=8·00. 0·2068 ,, 10·3 c.c. nitrogen at 7° and 770 mm. N=6·12. C_{12}H_{10}O_4N requires C=59·75; H=7·88; N=5·80 per cent.
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Properties of Ethylic Methylayanosuccinates.—The ethylic methylcyanosuccinates are colourless oils, and when pure are practically
odourless. We have carefully determined the following constants for
each of them; (1) boiling point (to within one degree) at 20 mm.
pressure; (2) density at 0°, as compared with that of water at 4°;
(3) refractive index for sodium light. The results are given in
Table V:

	Boiling point at 20 mm.	d_0/d_4 .	μ _{Na.}
Ethylic β-methylcyanosuccinate	157159°	1·0959	1·4352
Ethylic αβ-dimethylcyanosuccinate		1·0791	1·4368
Ethylic ββ- ,, ,,		1·0742	1·4363
Ethylic trimethylcyanosuccinate		1·0628	1·4418

TABLE V .- Properties of Ethylic Methylcyanosuccinates.

E. Hydrolysis of Ethylic Methylcyanosuccinates; Examination of the Resulting Succinic Acids.

After trying the action of various hydrolytic agents on the ethylic methylcyanosuccinates obtained as described in the preceding section we came to the conclusion that strong hydrochloric acid is the best

for the purpose of obtaining good yields of the corresponding succinic acids. We accordingly adopted the following method.

The ethylic cyanosuccinate was in each case boiled with six or eight times its volume of strong hydrochloric acid in a reflux apparatus on a sand-bath until the whole of the oil had disappeared. During the process, the cyanosuccinate was completely resolved into the corresponding succinic acid with evolution of carbonic anhydride as indicated in the earlier part of the paper (p. 846). On cooling the liquid, a portion, sometimes the greater part, of the acid crystallised out; this was collected by the aid of the pump, quickly washed with strong hydrochloric acid, recrystallised from the same solvent, dried at 100°, and weighed.

The filtrate was made alkaline with strong ammonia, filtered from any gelatinous silica, which usually separated at this stage, and the clear solution of ammonium salts boiled with excess of a 25 per cent. solution of calcium chloride. The insoluble calcium salt of the succinic acid was at once 'precipitated; this was collected by the aid of the pump, quickly washed with hot water, dried, first on a porous plate, then at 100°, and weighed. The amount of acid corresponding to it was calculated on the same basis as before. The salt was then decomposed by dissolving it in hot concentrated hydrochloric acid, and the acid which separated on cooling was collected at the pump.

It now remained in each case to see if any acid of the glutaric series was present in the filtrate from the insoluble calcium salt. The liquid was accordingly evaporated on the water-bath until there was just sufficient water left to retain all the ammonium chloride in solution at the ordinary temperature. A little more of the calcium salt of the succinic acid usually separated during the concentration, and was removed by filtering the hot liquid at the pump. The cold filtrate, to which an excess of hydrochloric acid had been added, was extracted five or six times with ether, the ethereal solution dried over anhydrous sodium sulphate, and the ether distilled off. In each case there was a small residue, never exceeding 1 gram in weight, which on long standing solidified, and after careful examination always proved to be a succinic acid. In no case were we able to detect any acid of the glutaric series among the products of hydrolysis, a proof that the ethylic methyl-cyanosuccinates contained no isomeric cyanoglutarates.

Having thus indicated the general method adopted for the hydrolysis of the ethylic cyanosuccinates, we will proceed to give, as briefly as possible, particulars concerning each operation, together with a description of the acids obtained.

(1) Ethylic β -Methylcyanosuccinate was completely hydrolysed in 4 to 6 hours, and no acid separated on cooling. The acid twice recrystallised from benzene, melted at 111° , and was identical with

monomethylsuccinic acid; the yield amounted to 80 per cent. of that theoretically obtainable. Analysis of the acid:

0.14 gave 0.2344
$$CO_2$$
 and 0.0782 H_2O . $C = 45.66$; $H = 6.20$. $C_3H_8O_4$ requires $C = 45.45$; $H = 6.06$ per cent.

(2) Ethylic aβ-Dimethylcyanosuccinate was hydrolysed in 15 to 20 hours. On cooling, the insoluble trans-s-dimethylsuccinic acid separated, the cis-acid remaining in solution. The last named was isolated by means of its insoluble calcium salt in the manner already described. The cis- and trans-acids were thus obtained in practically equal quantities, the total yield being 70 per cent. of that theoretically possible.

*trans-s-Dimethylsucoinic Acid.—The crude acid melted at 188—195°, but after recrystallisation from benzene at 194—197°. It evidently still contained a small quantity of the cis-acid, and was therefore treated in the cold with acetyl chloride, in order to remove this impurity as anhydride. The residual acid now melted at 203—208°, and after a second treatment with acetyl chloride, melted very sharply at 209°. On analysing it, the following results were obtained:

0.2017 gave 0.3628 CO₂ and 0.1271 H₂O.
$$C=49.08$$
; $H=7.00$. $C_6H_{10}O_4$ requires $C=49.31$; $H=6.84$ per cent.

Analysis of the silver salt:

0.3264 gave 0.1960 Ag. Ag = 60.10 per cent. $C_6H_9O_4Ag$ requires Ag = 60.00 per cent.

cis-s-Dimethylsuccinic Acid, after several recrystallisations from strong hydrochloric acid, melted at 128—129°.

0.1996 gave 0.3601 CO₂ and 0.1303 H₂O. C = 49.18; H = 7.25. $C_6H_{10}O_4$ requires C = 49.31; H = 6.84 per cent.

Analysis of the silver salt:

0.3841 gave 0.2786 CO_2 , 0.0795 H_2O , and 0.2300 Ag. C = 19.79; H = 2.30; Ag = 59.86.

0.2772 gave 0.1659 Ag. Ag = 59.89.

 $C_6H_8O_4Ag_2$ requires C = 20.00; H = 2.22; Ag = 60.00 per cent.

* In a previous paper (Bone and Perkin, Trans., 1896, 69, 253), one of us gave 209° as the melting point of this acid, pointing out at the same time that other workers had found that it melted at various temperatures between 188° and 194°. Quite recently, Fittig (Annalen, 1899, 805, 177) gave 197—198° as the melting point of the trans-s-dimethylsuccinic acid obtained by the reduction of dimethylsumaric acid with sodium analgam, and states that he was quite unable to confirm the higher melting point, that is, 209°. We have therefore paid particular attention to the matter. It is extremely difficult to effect a complete separation of the cis- and trans-acids by crystallisation from such solvents as water, benzene, &c.; hence the lower melting points assigned by Fittig and others to the trans-acid. The last trace of cis-acid may be completely removed as anhydride by treatment with acetyl chloride as described. The pure trans-acid melts at 209°.

¹⁴ (3) Ethylic $\beta\beta$ -Dimethylcyanosuccinate.—The hydrolysis was complete in about 15 hours, and the greater part of the as-dimethylsuccinic acid separated on cooling; the yield amounted to 80 per cent. of that theoretically obtainable. The acid, after being recrystallised from strong hydrochloric acid, melted at 140—141°, and on analysis gave the following numbers:

```
0.1399 gave 0.2536 CO<sub>2</sub> and 0.0890 H<sub>2</sub>O. C = 49.44; H = 7.06. 0.1145 , 0.2071 CO<sub>2</sub> , 0.0721 H<sub>2</sub>O. C = 49.31; H = 6.99. C_6H_{10}O_4 requires C = 49.31; H = 6.84 per cent.
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Analysis of the silver salt:

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0.2403 gave 0.1786 CO<sub>2</sub>, 0.0519 H<sub>2</sub>O, and 0.1442 Ag. C = 20.28; H = 2.39; Ag = 60.02.
```

 $C_6H_8O_4Ag_2$ requires C=20.00; H=2.22; Ag=60.00 per cent.

(4) Ethylic Trimethylcyanosuccinate required 40—45 hours for complete hydrolysis. Much acid separated on cooling, and the yield amounted to 80 per cent. of that theoretically obtainable. The trimethylsuccinic acid melted at 148° after several recrystallisations from hot concentrated hydrochloric acid, and on analysing it the following numbers were obtained:

Analysis of the silver salt:

0.3385 gave 0.2770 CO_2 , 0.0764 H_2O , and 0.1954 Ag. C = 22.32; H = 2.51; Ag = 57.60.

 $C_7H_{10}O_4Ag$ requires C=22.45; H=2.67; Ag=57.74 per cent.

The foregoing experiments show that the time required for the hydrolysis of an ethylic methylcyanosuccinate with strong hydrochloric acid under the same conditions increases considerably with the number of methyl groups in the molecule, a fact which is quite in accordance with the views of V. Meyer on the hydrolysis of ethereal salts.

We are now in a position to state the yields of methyl-substituted succinic acids obtainable from ethylic cyanacetate by the methods we have described. In order that a comparison may be readily made between this and the methods already discussed, the following numbers express the yields of ethylic methylcyanosuccinates and the corresponding succinic acids actually obtained in our experiments, in terms of the quantities theoretically possible from the amount of ethylic cyanacetate used in each case.

Pe	r cen	t. P	er cent
1	yield.		yield.
Ethylic β-methylcyanosuccinate	70	Monomethylsuccinic acid	56
,, aß-dimethylcyanosuccinate	52	s-Dimethylsuccinic acids	36
,, ββ-dimethylcyanosuccinate.	60	as-Dimethylsuccinic acid	48
,, trimethylcyanosuccinate	54	Trimethylsuccinic acid	48

F. Anhydrides, Anilic Acids, and Insoluble Calcium Salts of Methyl-substituted Succinic Acids.

Methyl-substituted succinic acids can be most readily identified by means of their anhydrides, anilic acids, and characteristic insoluble calcium salts. The last named, more especially, enable us to distinguish at once between a methyl-substituted succinic acid and an isomeric acid of the glutaric series. We have therefore submitted these derivatives to a very thorough examination, in order that other workers may have data whereby they may characterise any supposed methylsuccinic acid.

The anhydride was in each case prepared by dissolving the acid in $l\frac{1}{2}$ times its weight of acetyl chloride. After the evolution of hydrochloric acid had ceased, the solution was heated in a reflux apparatus on the sand-bath for 2 to 3 hours, then placed in a vacuum over solid potash, and after the excess of acetyl chloride had volatilised, the residue was fractionally distilled under diminished pressure. The portion of higher boiling point consisted of the pure anhydride in the form of a colourless oil which usually solidified on standing for a short time in a vacuum over sulphuric acid.

The anilic acid was in each case prepared from the anhydride by dissolving it in benzene, and mixing this solution with rather more than the calculated quantity of freshly distilled aniline, also dissolved in benzene. Much heat was evolved, and the anilic acid crystallised out on cooling as a white solid, which was collected at the pump, washed with cold benzene, and finally recrystallised either from hot dilute alcohol or an excess of hot benzene.

The calcium salt of each acid was precipitated by boiling an ammoniacal solution of the ammonium salt with a slight excess of a 25 per cent. solution of calcium chloride. It was then collected at the pump, washed with water, and dried either between filter paper or at 100° in a steam oven. The water of crystallisation, which was quickly

* Unsymmetrical succinic acids, as for example, the monomethyl, as-dimethyl, and trimethyl derivatives, should, of course, give two isomeric anilic acids; we have, however, only been able to obtain one from each anhydride by the method described. In this connection, it may be mentioned that only one of the two possible methylic hydrogen salts of such acids is produced when their anhydrides are dissolved in methylic alcohol.

expelled at a temperature of 140—150°, and also the amount of calcium oxide left on ignition of the anhydrous salt, were then estimated.

We may here remark that all these calcium salts, except that of trans-s-dimethylsuccinic acid, contain water of crystallisation. Our experiments show that in certain cases, as, for example, the calcium salts of the monomethyl and trimethyl acids, a part of this water of crystallisation is expelled at a temperature of 100°, the remainder requiring a higher temperature (140—150°) for its expulsion. In other cases, samples of the salt dried at 100° have exactly the same composition as those dried at ordinary temperatures between filter paper under pressure.

Monomethylsuccinic Acid, m. p. 111°.

Anhydride.—A liquid which began to crystallise on standing in a vacuum over sulphuric acid at 0° for many days. The crystals melted somewhere between 5° and 10°.

0.2471 gave 0.4739 CO_2 and 0.1189 H_2O . C = 52.30; H = 5.34. $C_5H_6O_8$ requires C = 52.63; H = 5.26 per cent.

Anilic Acid melted at 148-149°.

0.1851 gave 0.4303 CO₂ and 0.1059 H₂O. C = 63.40; H = 6.34.

0.2356 , 13.8 c.c. nitrogen at 13° and 754 mm. N = 6.86.

 $C_{11}H_{18}O_8N$ requires C = 63.76; H = 6.28; N = 6.76 per cent.

Calcium Salt.—(a) Dried for 24 hours between filter paper under pressure.

- 0.9487 lost 0.2296 H_2O at 140—150°. $H_2O = 24.20$ per cent. $C_5H_6O_4Ca + 3H_2O$ requires $H_2O = 24.11$ per cent.
- (b) Dried at 100°.
 - 0.6148 lost 0.1086 H_2O at 140—150°. $H_2O = 17.66$ per cent. $C_5H_6O_4Ca + 2H_9O$ requires $H_9O = 17.48$ per cent.
- (c) Anhydrous salt.
 - 0.3044 gave, on ignition, 0.1009 CaO. CaO = 33.14. $C_5H_6O_4$ Ca requires CaO = 32.94 per cent.

tran -- s-Dimethylsuccinic Acid, m. p. 209°.

Anhydride melted at 41-43° after recrystallisation from benzene.

0.1359 gave 0.2816 CO₂ and 0.0783 H_2O . C = 56.51; H = 6.43. $C_6H_8O_3$ requires C = 56.25; H = 6.25.

Anilic acid melted at 169-171°.

0.1344 gave 0.3205 CO₂ and 0.0836 H₂O. C=65.01; H=6.91. 0.3789 ,, 20.5 c.c. nitrogen at 15° and 762 mm. N=6.36.

 $C_{12}H_{15}O_3N$ requires $C=65\cdot15$; $H=6\cdot78$; $N=6\cdot33$ per cent.

Calcium salt, anhydrous.

0.2915, on ignition, gave 0.0883 CaO. CaO = 30.30. $C_6H_8O_4Ca$ requires CaO = 30.43 per cent.

cis-s-Dimethylsuccinnic Acid, m. p. 128°.

Anhydride melted at 91° after being twice recrystallised from benzene.

0.1878 gave 0.3922 CO₂ and 0.1094 H₂O. C = 56.34; H = 6.44. $C_6H_8O_8$ requires C = 56.25; H = 6.25 per cent.

Anilic Acid melted at 136-137°.

0.2081 gave 0.4986 CO₂ and 0.1304 H₂O. C = 65.33; H = 6.96. 0.2273 ,, 11.9 c.c. nitrogen at 15° and 748 mm. N = 6.31. $C_{12}H_{15}NO_3$ requires C = 65.15; H = 6.78; N = 6.33 per cent.

Calcium Salt.—(a) Dried at 100° gave the following numbers:

0.3002 lost 0.0485 H_2O at 140—150°. $H_2O = 16.16$. $C_6H_8O_4Ca + 2H_2O$ requires $H_2O = 16.36$ per cent.

(b) Anhydrous salt.

0.2772, on ignition, gave 0.0840 CaO. CaO = 30.29. $C_8H_8O_4Ca$ requires 30.43 per cent. CaO.

as-Dimethyleuccinic Acid, m. p. 140-141°.

Anhydride melted at 31°.

0.1675 gave 0.3431 CO₂ and 0.0962 H₂O. C = 56.19; H = 6.40. $C_6H_8O_8$ requires C = 56.25; H = 6.25 per cent.

Anilic Acid melted at 186-187°.

Calcium Salt.—(a) Dried between filter paper at the ordinary temperature.

 $0.8486 \text{ lost } 0.0800 \text{ H}_2\text{O} \text{ at } 140-150^{\circ}. \text{ H}_2\text{O} = 9.42 \text{ per cent.}$

- (b) Dried at 100°.
 - 0.6302 lost 0.0707 at 140—150°. $H_2O = 8.91$ per cent. $C_6H_8O_4Ca + H_2O$ requires $H_2O = 8.91$ per cent.
- (c). Anhydrous salt.

0.7639, on ignition, gave 0.2325 CaO. CaO = 30.43.

 $C_6H_8O_4Ca$ requires CaO = 30.43 per cent.

Trimethyleuccinic Acid, m. p. 148-149°.

Anhydride melted at 38°.

0.1631 gave 0.3520 CO₂ and 0.1071 H₂O. C=58.84; H=7.29. $C_7H_{10}O_8$ requires C=59.15; H=7.11 per cent.

Anilio Acid melted at 135°.

0.2102 gave 0.5096 CO₂ and 0.1395 H₂O. C=66·13; H=7·37.

0.3679 , 24 c.c. nitrogen at 16° and 745 mm. N = 5.89.

 $C_{18}H_{17}O_3N$ requires C = 66.34; H = 7.23; N = 5.95 per cent.

Calcium Salt.—(a) Dried at the ordinary temperature between filter paper.

- 0.2715 lost 0.0605 H_2O at 140—150°. $H_2O = 22.28$. $C_7H_{10}O_4Ca + 3H_2O$ requires $H_2O = 21.43$ per cent.
- (b) Dried at 100°.
 - $0.4373 \text{ lost } 0.0822 \text{ H}_2\text{O} \text{ at } 140-150^{\circ}. \quad \text{H}_2\text{O} = 18.8 \text{ per cent.}$ $C_7\text{H}_{10}O_4\text{Ca} + 2\frac{1}{2}\text{H}_2\text{O} \text{ requires H}_2\text{O} = 18.52 \text{ per cent.}$
- (c) Anhydrous salt.
 - 0.5369, on ignition, gave 0.1516 CaO. CaO = 28.24. $C_7H_{10}O_4Ca$ requires CaO = 28.28 per cent.
 - F. Dissociation Constants of the Methyl-substituted Succinic Acids.

In 1891, Walden (Zeit. physikal. Chem., 8, 433) determined the dissociation constants of the methyl-substituted succinic acids. Since that time, however, a great deal of work has been done on these bodies, and at least three of them, namely, the two s-dimethyl and the trimethyl acids, can now be prepared in a much purer condition than was then possible. Seeing, moreover, that the new method we have described in this paper enables us to prepare substituted succinic acids absolutely free from any isomeric acids of the glutaric series, it seemed desirable that we should redetermine their dissociation

constants. This we accordingly did, and our results, as will be seen, agree very well with those of Walden.

In the following tables,

v = number of litres which contain 1 gram-molecule of the acid.

 $\mu_v = \text{molecular conductivity at the dilution } v.$

 μ_{∞} = molecular conductivity at infinite dilution.

m =degree of dissociation μ_v/μ_{∞} .

$$k = \frac{m^2}{(1-m)v}$$
; $K = 100 k$.

All the determinations were made at a temperature of 23°.

Monomethylsuccinic Acid, m. p. 111°. $\mu_{\infty} = 354$.

v.	μ,.	m.	<i>K</i> .
50	22.14	0.0625	0.00833
100	3 1· 1 8	0.0881	0.00851
200	43.58	0.1231	,0.00864
400	60.17	0.1700	0.00870

Mean, K = 0.00854. Walden gives K = 0.0086.

trans-s-Dimethylsuccinic Acid, m. p. 208°. $\mu_{\infty} = 352$.

v.	$\mu_{\mathbf{p}}$	m.	K.
32	26.51	0.0753	0.0191
64	37.02	0.1051	0.0193
128	52.16	0.1482	0.0201
256	72.00	1.2046	0.0205

Mean, K = 0.0196. Walden gives K = 0.0191 for acid, m. p. 194°.

cis-s-Dimethylsuccinic Acid, m. p. 128°. $\mu_{\infty} = 352$.

v.	μ_{v} .	m.	<i>K</i> .
64	29.98	0.0852	0.01240
128	41.73	0.1185	0.01242
256	57 ·50	0.1634	0.01247
512	77:41	0.2199	0.01211

Mean, K = 0.01235. Walden gives K = 0.0123 for acid, m. p. 120°.

as-Dimethylsuccinic Acid, m. p. 140°. $\mu_{\infty} = 352$.

v.	μ_{\bullet} .	m.	<i>K</i> .
32	17.40	0.0494	0.00802
64	24.41	0.0693	0.00806
128	34·01	0.0966	0.00806
256	47.10	0·13 3 8	0.00808

Mean, K = 0.00805. Walden gives K = 0.0080.

Trimethylsuccinic Acid, m. p. 148°. $\mu_{co} = 350$.

υ.	μ.,	m.	K.
32	33.66	0.0956	0.0316
64	47.28	0.1344	0.0326
128	64.66	0.1837	0.0323
256	87.68	0.2491	0.0322

Mean, K = 0.0321. Walden gives K = 0.0307 for acid, m. p. 139.5°.

In Table VI, we give the properties of the methyl-substituted succinic acids, their insoluble calcium salts, anhydrides, and anilic acids:

TABLE VI.

Acid.	М, р.	Dissociation constant, <i>K</i> .		M. p. an- hydride.	M. p. anilic acid.
Monomethylsuccinic	111°	0.00854	$ \left\{ \begin{matrix} C_{5}H_{6}O_{4} + 3H_{2}O \\ C_{5}H_{6}O_{4} + 2H_{2}O \\ \text{at } 100^{\circ} \end{matrix} \right\} $	between 5°and 10°	148—149°
trans-s-Dimethyl- succinic	209°	0.0196	C ₆ H ₈ O ₄ ,Ca	41—43°	169—171°
cis-s-Dimethyl- succinic	128—129°	0.01235	$C_6H_8O_4Ca+2H_2O$.	91°	136—137°
as-Dimethylsuccinic	140—141°	0.00805	$C_6H_8O_4Ca+H_2O$	31°	186—187°
. Trimethylsuccinic	148°	0.0321	$ \begin{pmatrix} C_7 H_{10} O_4 Ca + 3 H_2 O \\ C_7 H_{10} O_4 Ca + 2 \frac{1}{2} H_2 O \\ at 100^5 \end{pmatrix} $	38°	1 35°

One of us, in conjunction with Dr. J. J. Sudborough, is engaged on an investigation of the hitherto little known methylic hydrogen salts of substituted succinic acids, and also in an attempt to resolve one of the s-dimethyl- and trimethyl-succinic acids into their active components. Finally, we are studying the interaction of the sodium derivatives of ethylic cyanosuccinates and the ethylic salts of a-bromofatty acids. The results of these various investigations will in due course be communicated to the Society.

OWENS COLLEGE,
MANCHESTER.

LXXXI.—Some Derivatives of Dibenzyl Ketone.

By Francis E. Francis, B.Sc., Ph.D., Lecturer in Chemistry, University College, Bristol.

R. Schiff has shown (Ber., 1898, 31, 205, 601, 1304, 1388; 1899, 32, 332), that benzalaniline forms additive products with acetoacetic ester and similar substances, giving, under certain conditions, three isomeric products. These, he considers, correspond with the ketonic, enolic, and keto-enolic forms of the original substance. When acetoacetic ester itself is used, equal molecules generally give rise to an additive product corresponding with different mixtures of the two desmotropic forms of the ester; the melting point lies between 95° and 100°, but in two cases was as high as 103-104°, pointing to the fact that the ester consisted of the pure enolic modification. When two molecules of the ester are mixed with one of benzalaniline, the resulting substance melts at 103°, and corresponds with the enolic form. A trace of piperidine introduced in the second case gives the third isomeride, melting at 78°, and corresponding with the ketonic modification of the ester. A trace of sodium ethylate changes this back to the enolic form, melting at 103°. That acetoacetic ester itself and the additive products melting at higher temperatures contain the enolic group is shown by the fact that they give reddish-blue colorations with ferric chloride. Dibenzyl ketone gives no colour reaction with this reagent; now, if the ferric chloride reaction for the enolic modification holds with such compounds, this might be taken as showing the absence of any such form in the original substance. When an alcoholic solution of the sodium salt is poured into dilute sulphuric acid at a temperature of -10° , the ketone that separates certainly gives a dark coloration with ferric chloride, which rapidly disappears, but the result is not sufficiently definite for any conclusions to be drawn.

Dibenzyl Ketone and Benzalaniline.

1. When equal molecules, or two molecules of the ketone to one of benzalaniline, are mixed together, a syrup is obtained which slowly solidifies; when this is dried on a porous plate and recrystallised from boiling benzene, the additive product separates out, on cooling, as a mass of silky needles, giving no reaction with ferric chloride, melting at 164.5° , and yielding the following data on analysis:

Found C = 86.31; H = 6.41; N = 3.82.

 $C_{28}H_{25}ON$ requires C=85.93; H=6.39; N=3.58 per cent. VOL. LXXV. A molecular weight determination by the boiling point method, using benzene as solvent, gave 413, the calculated value being 391.

2. When a trace of piperidine is added to either of the above mixtures, and, after solidification and drying, the mass is recrystallised from benzene, crystals melting at 174.5° are obtained. The same substance can also be produced by recrystallising the additive product melting at 164.5° from benzene containing a trace of piperidine. It gives no reaction with ferric chloride. On analysis, the following figures were obtained:

Found C = 86.14; H = 6.47. $C_{98}H_{98}ON$ requires C = 85.93; H = 6.39 per cent.

A molecular weight determination by the boiling point method gave 403, the calculated value being 391.

3. When either of the mixtures of dibenzyl ketone and benzalaniline is treated with a trace of sodium ethylate, the additive product, after recrystallisation, melts at 164.5°, but if this form, or that melting at 174.5°, is recrystallised several times from benzene containing a trace of sodium ethylate, the third isomeride, melting at 182.5°, is obtained. This modification is similar to the others in appearance, and, like them, gives no colour reaction with ferric chloride. It gave the following data on analysis:

Found C = 86.27; H = 6.40. $C_{ee}H_{ee}ON$ requires C = 85.93; H = 6.39 per cent.

Repeated crystallisation, and even fractional crystallisation, did not alter the melting points of the three modifications.

The question then arises, supposing these substances are analogous to those of Schiff, of assigning to them a constitution. Schiff states that "Spuren von Piperidin ketisiren die Enolformen, Spuren von Nahrumäthylat Enclisiren die Ketoformen." If such is the case, then presumably the second substance melting at 174.5° is the ketonic form, and that melting at 182° the enolic. That melting at 164.5° would then correspond with the mixed form, but there appears to be no evidence for this view, since the two forms melting at 182.50 and 174.5°, on being mixed and recrystallised, show an intermediate melting point. Moreover, if the original substance consisted of a mixture of the enolic and ketonic modifications, it might be supposed that a trace of sodium ethylate would have been sufficient to alter the equilibrium of the two forms, giving a preponderance of enolic molecules, which, in their turn, with benzalaniline, would have given the enolic compound melting at 182.5°, or at least have raised the melting point of the additive compound; but the presence of sodium ethylate was shown to have no effect on the resulting compound, the substance

melting at 182.5° being only formed by the action of the ethylate on either of the other two.

On the other hand, if dibenzyl ketone consists of the pure ketonic modification, which appears highly probable from its reactions, the substance melting at 164.5° is the ketonic, and presumably that melting at 174.5° is the mixed, form; but here, again, if equal molecules of the lowest and highest melting points are recrystallised from boiling benzene and light petroleum, in which both are insoluble in the cold, the resulting crystals melt at 173.5—174°, but are easily decomposed into their components by further crystallisation from benzene, whereas the melting point of the substance obtained by the action of piperidine remained constant at 174.5° after repeated recrystallisation.

Deoxybenzoin and Benzalaniline.

Analogous substances are being investigated, in the hope of elucidating the problem. Deoxybenzoin, for instance, behaves in a very similar way to dibenzyl ketone. It gives no reaction with ferric chloride; an alcoholic solution of the sodium salt, poured into dilute sulphuric acid at -10° , regenerates the ketone, which has the same melting point, and also gives no reaction with ferric chloride. If this test is relied on, then the substance appears to consist only of the ketonic modification.

1. When equal molecules of deoxybenzoin and benzalaniline are mixed together and kept at a temperature slightly above their melting point, the additive compound slowly separates out, the mass becoming solid. On recrystallising from a mixture of benzene and light petroleum or of chloroform and light petroleum, small, colourless needles are formed melting at 154°. The following data were obtained on analysis:

Found C = 86.18; H = 6.05.

 $C_{27}H_{28}NO$ requires C = 85.94; H = 6.10 per cent.

2. If a trace of piperidine is added to the above mixture, besides the second modification melting about 166° which separates, there is a certain quantity of a much less soluble substance crystallising from boiling toluene in needles exactly the same in appearance as the preceding substance melting at 188.5°. The quantity so far obtained was not sufficient for satisfactory purification, but an analysis of the fairly pure substance seemed to indicate that it had the same composition as the other modifications. The best method for obtaining the second isomeride is to dissolve the first, melting at 154°, in chloroform containing a trace of piperidine, and after some hours to precipitate the compound from solution by light petroleum; in this way, crystals

3 м 2

showing a perfectly constant melting point of 164—165° are obtained. The following figures were obtained on analysis.

Found C = 85.88; H = 6.09. $C_{97}H_{98}NO$ requires C = 85.94; H = 6.10 per cent.

3. The third isomeride is obtained by dissolving either of the preceding modifications in benzene, adding a trace of sodium ethylate, allowing to stand for 24 hours, and then precipitating by light petroleum. As in the case of dibenzyl ketone, it is not formed when sodium ethylate is added to equal molecules of the ketone and benzalaniline, either alone or in benzene solution. It forms needles similar in appearance to the others and melting at 172.5°, the melting point remaining constant on repeated recrystallisation.

An analysis gave the following data:

Found C = 85.29; H = 6.20.

 $C_{27}H_{28}NO$ requires C = 85.94; H = 6.10 per cent.

These substances are being further investigated and will form the subject of a future communication. It will be seen that the results are quite analogous to those obtained with dibenzyl ketone, except for the formation of the less soluble substance of higher melting point.

Dibenzyl Ketoxime.

The oxime prepared in the usual way showed a melting point of 125° instead of 119.5° as given by Rattner (*Ber.*, 1888, 21, 1316), a difference undoubtedly due to the greater purity of the ketone. On reduction with stannous chloride, it gives dibenzyl ketone.

Dibenzyl Ketone Phenylhydrazone, (C6H5CH2)2C:N·NHC6H5.

The phenylhydrazone is easily prepared by warming an alcoholic solution of phenylhydrazine and the ketone, when the condensation product separates out in well formed needles which are fairly soluble in boiling alcohol, soluble in cold ether, and melt at 128—129°. It is rapidly oxidised in contact with air, but may be kept unchanged in a vacuum even when exposed for months to bright sunlight.

Found N = 9.21. $C_{21}H_{20}N_2$ requires N = 9.33 per cent.

Action of Sodium Ethylate on Dibenzyl Ketone.

When sodium ethylate acts on an alcoholic solution of the ketone, one of the hydrogen atoms appears to be replaced to a certain extent by the sodium, the resulting sodium compound giving some benzyl a-ethylbenzyl ketone on treatment with ethylic iodide. Dibenzyl ketone is

dissolved in a small quantity of absolute alcohol and treated with the calculated quantity of sodium dissolved in alcohol, the necessary amount of ethylic iodide is then added, and the reaction, energetic at first, is complete in about one hour. The resulting solution is treated with water, and the oil that separates well washed. On distillation, the fraction coming over below 300° partially crystallises out on standing, but it was not found possible to separate the oils of higher boiling point. The oil, on treatment with hydroxylamine in alcoholic solution, gave an oxime melting between 90° and 93°, which on recrystallisation gave large, well-formed, transparent prisms melting at 106°, the melting point remaining constant on recrystallisation. From the analysis, this appears to be the oxime of benzyl α -ethylbenzyl ketone, C_0H_5 $CH_2C_3H_5$ $CH_2C_3H_5$

Found N = 5.64. $C_{17}H_{19}NO$ requires N = 5.53 per cent.

The crystals obtained in small amount from the first fraction, as above stated, proved, on analysis, to be the unsaturated hydrocarbon benzylphenylethylene, $C_6H_5 \cdot CH_2 \cdot CH \cdot C_6H_5$; it crystallises well from dilute alcohol, and is soluble in the ordinary organic solvents. It has a melting point of 57°, and boils at approximately 276°, as determined by Siwoloboff's method for small quantities of material. It gave the following figures on analysis:

Found C = 92.62; H = 7.54. $C_{15}H_{14}$ requires C = 92.78; H = 7.21 per cent.

A molecular weight determination by the boiling point method gave 170 instead of the calculated value, 194. The formation of this hydrocarbon is analogous to the formation of stilbene when deoxybenzoin is heated with sodium ethylate (Sudborough, Trans., 1895, 67, 604).

If a benzene solution of the hydrocarbon is treated with bromine, the corresponding dibromide, $C_6H_5 \cdot CH_2 \cdot CHBr \cdot CHBr \cdot C_6H_5$, separates out in small needles, which are best recrystallised from boiling benzene, dissolve only slightly in cold alcohol or acetic acid, and melt at 231° with immediate decomposition.

Found Br = 44.81. $C_{15}H_{14}Br_2$ requires Br = 45.19 per cent.

Action of Ammonia on Monobromodibenzyl Ketone.

Monobromodibenzyl ketone was prepared by Bourcart (*Ber.*, 1889, 22, 1368), and its melting point given as 43—44°. Using the same method, a good yield of bromodibenzyl ketone was obtained, and when

recrystallised from dilute alcohol and ether, the substance separated out as glistening needles melting at 49°.

When ammonia acts on a cold alcoholic solution of the substance, and the resulting solution is treated with water, a semi-solid mass is obtained. If this is dissolved in a small quantity of hot alcohol, the imido-compound, $NH[CH(C_6H_5)\cdot CO\cdot CH_2\cdot C_6H_5]_2$, crystallises out on cooling as white, silky needles. It is soluble in ether and benzene, but insoluble in light petroleum, and melts at 124°. It gave the following data on analysis:

Found C = 83.54; H = 6.28; N = 3.40. $C_{80}H_{e7}N$ requires C = 83.14; H = 6.23; N = 3.23 per cent.

On long standing, decomposition takes place, resulting in the formation of a yellow, insoluble substance possessing a high melting point. Its hydrochloride is obtained in the form of glistening needles by treating an alcoholic solution of the base with hydrochloric acid. It melts at 189° with decomposition, and is only slightly soluble in water.

If the alcoholic solution from which the above imido-compound has separated out is treated with a small quantity of water and the oil that separates is dissolved in ether, crystals of diphenyldibenzyldihydropyrazine, $C_6H_5 \cdot CH_2 \cdot C \cdot CH_2 \cdot C_6H_5 \cdot C \cdot CH_3 \cdot C_6H_5$, slowly separate in small quantity. These may be recrystallised from boiling alcohol or from glacial acetic acid, and is thus obtained in the form of small, white plates melting at 147°, which are almost insoluble in cold alcohol and slightly soluble in ether and benzene. A somewhat better yield is obtained by treating the bromide with a concentrated aqueous solution of ammonia and separating the mixture by the above means.

An analysis gave the following results: Found C = 87.30; H = 6.16; N = 7.03.

 $C_{80}H_{96}N_2$ requires C=86.95; H=6.28; N=6.77 per cent.

Action of Aniline on Bromodibenzyl Ketone.

When aniline and the bromo-derivative are warmed together, an energetic reaction takes place, resulting in the formation of the corresponding dianilide, C_6H_5 ·OH(NHC₆H₅)·C(:NC₆H₅)·CH₂·C₆H₅. If the mass so obtained is washed with dilute acetic acid and water to get rid of the excess of aniline and then recrystallised from boiling alcohol, small needles separate out on cooling. They are only slightly soluble in cold alcohol, soluble in ether, carbon bisulphide, and benzene, and melt at 127·5°.

Found N = 7.60, $C_{27}H_{24}N_2$ requires N = 7.44 per cent,

The hydrochloride, formed by warming an alcoholic solution with hydrochloric acid is almost insoluble in water and melts at 176°.

I have in conclusion to thank Professor S. Young for placing at my disposal some of the dibenzyl ketone prepared by his method (Trans., 1891, 59, 623).

LXXXII.—Action of Light and of Oxygen on Dibenzyl Ketone.

By EMILY C. FORTEY, B.Sc.

It was noticed by Professor S. Young in 1896 that a quantity of dibenzyl ketone, which had been prepared by him in 1891 and kept in stoppered vessels, had undergone partial decomposition, and that the action was the greatest in the case of those specimens which had been most exposed to light. At his suggestion, I undertook to investigate the action.

A considerable quantity of an acid vellow liquid had formed in the flasks containing the ketone. This was poured off, treated with sodium carbonate solution, extracted with ether, and the ethereal solution dried. After distilling off the ether, a small quantity of an oily liquid, giving the reactions of benzaldehyde and having its characteristic odour, came over below 250°, after which the temperature rose rapidly to the boiling point of dibenzyl ketone. The solution was acidified with hydrochloric acid, when a white, crystalline precipitate immediately formed; the liberated acids were extracted with ether and the ethereal solution was dried. After distilling off the ether, the residue solidified on cooling, and proved to be a mixture of benzoic and phenylacetic acids. After repeated fractional crystallisation from water, benzoic acid melting at 120° was obtained. Pure phenylacetic acid melting at 76° was also isolated from the mixture by recrystallisation from light petroleum. It seems probable that the ketone is first oxidised to a mixture of phenylacetic acid and benzaldehyde, according to the equation:

$$(\mathbf{C_6H_5 \cdot CH_2})_2\mathbf{CO} + \mathbf{O_2} = \mathbf{C_6H_5 \cdot CH_2 \cdot COOH} + \mathbf{C_6H_5 \cdot CHO},$$

and that the latter is then oxidised to benzoic acid.

In order to test the action of heat in absence of light, a sealed tube containing pure recrystallised dibenzyl ketone and filled with oxygen was heated to 100° in a steam chamber for ten days. The contents of the tube had then become yellow, and gave an acid reaction when tested with litmus. A tube containing dibenzyl ketone, and ex-

hausted of air, was treated similarly, but the contents remained unchanged. A second exhausted tube was then heated for some days in the vapour of boiling quinoline, but no decomposition of any sort took place. This harmonises with the fact, previously noted by Professor Young, that dibenzyl ketone may be used for some time as a jacketing agent without sensible alteration, the reason no doubt being that the contact with air is so small.

With a view to ascertain whether the oxidation of dibenzyl ketone would take place in absence of moisture, some crystals were placed in one limb of a bent tube, the other containing phosphorus pentoxide. After passing a current of dry air, the tube was sealed and kept in the dark for three weeks: it was then exposed to light. In a fortnight's time, the crystals had a decided yellow tinge, and after some months they had become deep yellow, and the liquid had an acid reaction, showing that absence of moisture had not prevented the decomposition of the ketone from taking place. A similar experiment was made, keeping the tube in the dark for nine weeks to ensure complete freedom from moisture, and then sealing off the limb containing the dibenzyl ketone and exposing it to sunlight. The result corroborated that obtained in the former experiment, marked decomposition taking place in a few months' time.

So far the decomposition of dibenzyl ketone observed had been due to the presence of oxygen. An experiment was now made to test the stability of the ketone in the absence of oxygen. Two tubes containing pure dibenzyl ketone were exhausted of air, a third was filled with carbon dioxide in place of air, and, for the sake of comparison, a fourth containing the ketone was filled with oxygen. All four tubes were exposed in a garden for two years. On opening the tubes, they were all found to contain carbon monoxide, which burnt with its characteristic blue flame, and toluene boiling at 110°, and yielding dinitrotoluene on nitration.* In addition, they all contained a white, solid substance, insoluble in water, alcohol, ether, carbon bisulphide. benzene, &c., but readily soluble in chloroform. It melted at 193-194°, and gave the following result on analysis:

0.1464 gave 0.4603 CO₂ and 0.0818 H₂O. C = 85.75; H = 6.21. $C_{30}H_{26}O_2$ requires C = 86.12; H = 6.22 per cent.

The quantity at my disposal was unfortunately too small to allow of an accurate determination of the molecular weight, but it seems most probable that two molecules of the ketone combine together with loss of hydrogen.

^{*} The formation of carbon monoxide and toluene on heating dibensyl ketone to 860° was observed by Engler and Löw (Ber., 1893, 26, 1488).

The action may possibly be represented by the equation:

$$3(C_6H_5 \cdot CH_2)_2CO = 2C_6H_5 \cdot CH_8 + CO + (C_{14}H_{13} \cdot CO)_2$$

This was the only action observed in the case of the dibenzyl ketone in the exhausted tube, and in the tube containing carbon dioxide, the contents of both of which remained colourless, but in the case of the tube filled with oxygen, the ordinary decomposition into benzaldehyde, benzoic acid, and phenylacetic acid had also taken place, and the contents were deep yellow in colour. The tendency of dibenzyl ketone to undergo oxidation is in marked contrast to the behaviour of benzophenone, which is one of the most stable substances known.

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LXXXIII.—The Vapour Pressures, Specific Volumes and Critical Constants of Hexamethylene.

By SYDNEY Young, D.Sc., F.R.S., and EMILY C. FORTEY, B.Sc.

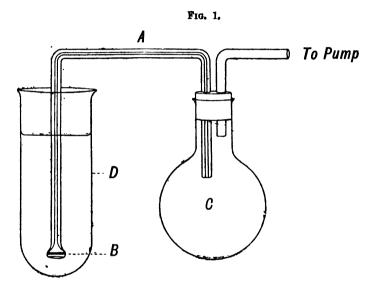
A small quantity of hexamethylene was obtained by one of us (Trans., 1898, 73, 932) by the long-continued fractional distillation of Galician petroleum. The liquid boiled quite constantly at 80.8° ; its specific gravity at $0^{\circ}/4^{\circ}$, 0.7903, agreed perfectly with that of a specimen prepared synthetically by Markownikoff (Annalm, 1898, 302, 1), and the results obtained on analysis were quite satisfactory. The fraction with the constant boiling point was also the one that possessed the highest specific gravity. For these reasons, the specimen was regarded as pure. When the vapour pressures of the hexamethylene at low temperatures were being determined by the method of Ramsay and Young, it was noticed that partial solidification took place in the condenser, which was cooled by a freezing mixture. It thus became evident that the substance had a higher freezing point than had previously been supposed. It was found, however, to be far from constant—say -12° to -7° —depending on the relative quantities of solid and liquid.

It is clear, then, that hexamethylene from petroleum contains a certain amount of a hydrocarbon, probably a heptane such as trimethylpropylmethane, boiling at a temperature near to 81°, and inseparable from the hexamethylene by fractional distillation.

It seemed probable that the impurity might be removed by fractional crystallisation, but as the amount of material was very small, we thought it advisable to utilise, if possible, the less pure fraction (76—78.5°) left over after the chemical investigation of hexamethylene had been completed (Trans., 1898, 73, 932).

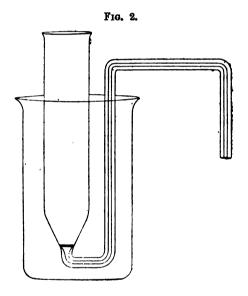
This liquid was first redistilled with a 12 column Young and Thomas dephlegmator, when the greater portion came over between 77.5° and 80°. A partial purification of this fraction was effected by treatment with chlorosulphonic acid (Trans., 1899, 75, 172), both the boiling point and specific gravity being thereby raised, whilst the freezing point became sufficiently high to admit of partial solidification in a mixture of solid carbon dioxide and ether.

The separation of the crystals from the mother liquor was effected by means of the apparatus shown in Fig. 1. A piece of thick-walled



tubing, A, of about $1\frac{1}{3}$ mm. bore was bent twice at right angles; one end, B, was enlarged into a small funnel into which were fused three circular pieces of platinum gauze as nearly as possible in contact with each other. The other limb of the tube was connected with a round bottomed flask, C, which could be exhausted. The liquid was first partially frozen in the open tube, D, and the tube A was then placed in position as shown in the diagram, and the pump set in action. The meshes of the gauze effectually prevented the passage of the crystals, although they were exceedingly small, and the residue appeared hard and snowy, notwithstanding that, owing to its porous nature, it still retained a considerable amount of liquid impurity. The residue, after fusion, was partially solidified by means of a freezing mixture containing more ether, and this operation was continued until the freezing point of the hexamethylene had risen above -40° , when a second apparatus (Fig. 2) was employed.

This apparatus consisted of a wide, cylindrical tube drawn out below and fused to a thick-walled tube of narrow bore, bent four times at right angles. Three pieces of platinum gauze were fused into the wide tube just above the junction with the narrow one. Mercury was poured into the vessel until it rose well above the platinum gauze, and the narrow tube was connected with a round-bottomed flask, which, as before, was attached to a pump. The liquid to be frozen was then placed in the wide tube, and was cooled by a suitable freezing mixture, such a temperature being always chosen that only partial solidification could take place. After the solidification had reached its limit, the bulb was exhausted, when the mercury, followed by the mother liquor, was carried over into it, the residue meanwhile being well pressed



down. This apparatus is more effective than the first, but can obviously only be used for temperatures above the freezing point of mercury. By a series of fractional crystallisations carried out as described, a quantity of hexamethylene was obtained equal in purity to the best specimen; the fractions were then mixed together, and the further purification proceeded with.

After a few more recrystallisations, ice could be used as the freezing agent, and the melting point finally rose to 4.7°. Although there was still a slight fall of temperature before solidification was complete, this may be taken as very close indeed to the true melting point of hexamethylene, and our specimen may be regarded as so pure that the errors in the physical constants would be inappreciable.

Specific Gravity.

Owing to the readiness with which hexamethylene solidified at 0°, it was not possible to make a direct determination of the specific gravity at this temperature, but the constant was calculated from the volume of a gram read from a curve constructed from the observations at higher temperatures. The specific gravities were directly determined with a Sprengel tube, as modified by Perkin, at 10.7° and 14.5°; the weighings were in all cases reduced to a vacuum.

Temperature.	Specific gravity
0 °	0.79675
10.7	0.78715
14.5	0.78280

Specific gravities by other observers.

Name.	Reference.	Sp. gr. at C.	Calc. at 0°/4°.*	
Brühl † Markownikoff ‡	Ber., 1894, 27, 1065. Ann., 1898, 802, 1.	0.790 at 20°/4° 0.7902 at 0°/0°	0.8090 0.7901	
Zelinsky‡	Ber., 1895, 28, 1022.	0·7727 at 20°/0° 0·7764 at 20°/4°	0·7912 0·7951	

^{*} Assuming the expansion from 0° to 20° to be the same as for our specimen.

Our value agrees best with that of Zelinsky; the specimen used by Brühl must have contained some heavy impurity.

Boiling point.

Press.	Temp.	Corr. to 760 mm	n.
754·7	80·65°	80·9°	
759.75	80.8	80.8	
	1	F 00.05	

Calculated from the constants for Biot's formula, the boiling point is 80.9° , and the value of dp/dt at the boiling point = 22.75 mm. per degree.

⁺ Prepared synthetically by Basyer (Annalen, 1898, 278, 88).

[‡] Prepared synthetically.

Boiling points by other observers.

Name.	Boiling point.	Reduced to 760 mm.
Baeyer		· 79 —79·5°
Markownikoff		80· ŏ —81
Zelinsky	81-82° at 740 mm.	about 82 —83

Markownikoff's boiling point agrees well with ours, but Baeyer's is decidedly too low and Zelinsky's too high.

Vapour Pressures at Low Temperatures.

For pressures up to 270 mm., the method of Ramsay and Young was employed; from 153 mm. to the atmospheric pressure, a modified distillation bulb with reflux condenser was used.

Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.
19.95	- 5·85°	42.45	7 ·95°	101.65	26·2°	217.9	44.5°
20.95	- 4.50	49.9	11.2	115.35	29.05	243.1	47.3
23.05	- 3.02	58.0	14-25	182.4	32.25	272.8	50.45
26.7	- 0.20	68.05	17.5	153.05	85.65		
81.2	+2.20	78.25	20.7	178.1	38.65	ii.	
86.35	5.05	89.45	28.25	194.7	41.45	!! !	
158-5	85.55	242.4	47.25	373.4	59.0	559.5	71.0
178.1	88.45	271.0	50.15	409.6	61 .7	617.8	74.1
198.4	41.25	801.5	53.1	462-1	65.3	670.4	76.75
217.1	44.85	836.5	56.15	511.7	68.35	718.9	78.8

The vapour pressures at high temperatures were determined with the pressure apparatus employed by one of us in previous researches, and the usual corrections were made.

The observed pressures (the mean of four readings in each case), together with those read from the curves constructed from the observations at low temperatures, and also the pressures calculated by means of Biot's formula,

$$\log p = a + ba^t + c\beta^t$$

are given in the following table.

The constants for Biot's formula are:

$$a = 1.424527$$

$$b = 2.354051$$

$$c = -2.333778$$

$$\log c = 0.3680596$$

$$\log a = 0.00049715$$

$$\log \beta = 1.99608748$$

$$t = t^{\circ}C$$
Digitized by

Vapour pressures.

Temperature.	Dynamical method from curve.	Statical method.	Calculated from Biot's formula.	Temperature.	Statical method.	Calculated from Biot's formula.
0° 10	27·55 47·05		27·85 47·09	150° 160	4123 5028	4124·5 5007·8
20	76.9		76.58	170	6041	6021.9
80	121.35		120.16	180	7194	7199-9
40	181.65		182.49	190	8482	8494.5
50	269.2		269.05	200	9977	9980-2
60	385.0		886.07	210	11651	11651
70	540.8		540.51	220	18511	18526
80	741 .8		739 91	230	15601	15622
90	•	992	992:34	240	17978	17961
100		1304	1306.8	250	20529	20565
110		1687	1691 0	260	23439	28461
120		215 2	2155.4	270	26667	26680
130		2703	2709 1	277	29206	
140		3862	3362.0	279.95 (Critical)	80260	30234

The critical temperature was taken to be $280\cdot0^{\circ}$ and the critical pressure 30252 mm.

Volumes of a Gram of Liquid.

These were determined in the pressure apparatus; up to 180°, the volumes were read directly, but at higher temperatures they were

Volumes of a gram and molecular volumes of liquid.

m		of a gram.	M. ll.	ar Tempera-	Volumes e	Molecular	
Tempera- ture.	Observed.	From curve.	volumes.	ture.	Observed.	From curve.	volumes.
0° 10	_	1·2551 1·2700	105·20 106·45	170° 180	1·6131 1·6481	1.6130 1.6482	185 20 188·15
20		1.2855	100 45	190	1.6910	1.6875	141.45
30	1.3018	1.3012	109.07	200	1.7800	1.7802	145.08
40	1.3170	1.3174	110.43	210	1.7805	1.7775	148.99
50	1.3346	1.3341	111.83	220	1.8800	1.8327	153.62
60	1.3513	1.3514	113-27	230	1.8975	1.8970	159.01
70	1 3689	1.3688	114.78	240	1.9745	1.9750	165.55
80	1.3878	1.3878	116.33	250	2.0745	2.0745	178-90
90	1.4064	1.4073	117.96	260	2.2083	2.2060	184-9
100	1 4279	1.4279	119.69	265	2.2940	2.297	192.5
110	1.4508	1.4496	121.51	270	2.4240	2.424	203 · 2
120	1.4784	1.4726	123.43	274	2.5670	2.570	215.4
130	1.4970	1.4970	125.51	277	2.7470	2.746	230.2
140	1.5282	1.5233	127.69	279	2.9470	2.947	247.0
150	1.5507	1.5509	130.00	280	-	3.659*	806·7*
160	1.5811	1.5810	132.52				
			l		l		L

calculated from observations of the volume of vapour and the total volume of liquid and vapour by the method described by one of us in the Transactions (1893, 63, 1200).

The observed and smoothed specific volumes, and the molecular volumes calculated from the smoothed specific volumes, are given in the foregoing table.

The molecular weight is taken as 83.82.

Volumes of a Gram of Saturated Vapour.

Determinations were made with the pressure apparatus and by the sealed tube method (Trans., 1891, 50, 37; Phil. Mag., 1895).

The results are given in the table below, also the volumes of a gram read from curves constructed by plotting the logarithms of the volumes against the temperatures. The molecular volumes calculated from the smoothed specific volumes are also given.

Volumes of a gram and molecular volumes of saturated vapour.

Temperature.	Pressure	Sealed tul	From curves.	Molecular volumes.	
	apparatus.	I.	II.	From curves.	
. 90°		267		266	22300
100	.	203		204	17100
110		159		159	13300
120	i	125.5		125.5	10530
130		100.4]	100.0	8880
140	ŀ	80.9	İ	80.8	6775
150	İ	66·4 54·6	54.6	66·8 55·0	5560 4610
160 170		94.0	46.0	45.8	3840
180	•		38.4	88.1	30±0 3190
190	31.1		81.7	81.85	2670
200	26.9		26.8	26.75	2248
210	22.3		22.6	22.54	· 1890
220	19:20		19.0	19.05	1597
230	16.02		16.0	16.00	1841
240	13.38		13.32	13.34	1118
250	11.06		11.02	11.04	926
260	8.99		8.95	9.00	754
265	8.05		7.97	8.01	671
270	6.96		6.97	6.98	585
274	6.14		6.10	6.12	513
277	5.39			5.39	452
279	4.75		_	4.75	398
280 (Critical)	-		_	8.659*	306-7*

^{*} By the method of Cailletet and Mathias.

The critical volume of a gram and the molecular volume were calculated from the critical density, which was ascertained by the method of Cailletet and Mathias (*Compt. rend.*, 1886, 102, 1202; 1887, 104, 1563; 1892, 115, 35).

The densities of liquid and saturated vapour, the mean densities and those calculated from the formula $D_t = 0.3954 - 0.000436t$ are given below.

	Den	sities.	Mean densities.			
Temperature.	Liquid.	Saturated vapour.	Observed.	Calculated.	Δ×104	
90°	0.7106	0.0038	0.8572	0.3562	- 10	
100	0.7003	0.0049	0.3526	0.3518	-8	
110	0.6898	0.0063	0.8481	0.8474	-7	
120	0.6791	0.0080	0.3435	0.8431	-4	
130	0.6680	0.0100	0.8890	0.3487	- 3	
140	0.6565	0.0124	0.8844	0.8844	` ŏ	
150	0.6448	0.0121	0.3299	0.3300	+1	
160	0.6325	0.0182	0.8254	0.8256	+2	
170	0.6200	0.0218	0.8209	0.3213	+4	
180	0.6067	0.0262	0.3165	0.3169	+4	
190	0.5926	0.0314	0.3120	0.3126	+ 6	
200	0.5780	0.0374	0.3077	0.3082	+5	
210	0.5626	0.0444	0.8035	0.3038	+8	
220	0.5456	0.0525	0.2991	0.2995	+4	
230	0.5271	0.0625	0.2948	0.2951	+3	
240	0.5063	0.0750	0.2907	0.2908	+1	
250	0.4820	0.0906	0.2868	0.2864	+1	
260	0.4588	0.1112	0.2822	0.2820	-2	
265	0.4354	0.1249	0.2801	0.2799	- 2	
270	0.4125	0.1482	0.2779	0.2777	- 2	
274	0.3891	0.1683	9.2762	0.2759	3	
277	0.3642	0.1857	0.2749	0.2746	- 8	
279	0.3393	0.2105	0.2749	0.2788	- 11	
280		-		0.2733		
(Critical)						

It may be interesting to compare the critical and other constants of the hydrocarbons, benzene, hexamethylene, and normal hexane, as they all contain six atoms of carbon in the molecule, but differ essentially in constitution. The data are given in the following table:

Melting point	Benzene. 5.6°	Hexamethylene. 4.7°	N. Hexane.
Boiling point (760 mm.)	80·2°	80·9°	68·95°
Specific gravity 0°/4°	0.90000	0.79675	0.67697
Critical temperature	288·5°	280·0°	234·8°
Critical pressure in mm	36395	30252	22510
Critical density	0.3037	0.2733	0.2343
Critical volume of a gram	3.293	3.659	4.268
Critical molecular volume	256.3	306.7	366-3

In its behaviour with chemical reagents, hexamethylene shows a much closer resemblance to normal hexane than to benzene, but, on the other hand, in certain of its physical properties it exhibits a most striking relationship to benzene; thus their melting points and boiling points differ respectively by less than a degree, whilst the critical temperature of hexamethylene is only 8.5° lower than that of benzene, but is 45.2° higher than that of normal hexane. The specific gravity at 0°, the critical density, and the critical pressure of hexamethylene lie, however, about midway between those of the other two hydrocarbons.

The absolute temperatures and the molecular volumes of liquid and saturated vapour were read from the curves at a series of pressures "corresponding" to those given in previous papers; from these data, the ratios of the temperatures and volumes to the critical constants were calculated, also the ratios of the actual to the theoretical densities of saturated vapour.

For the sake of comparison, the ratios for benzene and normal hexane, the other two six-carbon hydrocarbons so far investigated, are given in addition to those of hexamethylene in the following tables:

Ratios to critical pressures.	Pressures.	Absolute tempera- tures.	Molecular volumes.		Ratios of actual to theoretical densities of saturated vapour.		
			Liquid.	Saturated vapour.	Hexa- methylene.	Benzene.	Normal hexane
0.001474	44.60	281 ·85°	106:30			!	
0.002949	89.21	296.05	108.14		ł	i	
0.005898	178.4	312-25	110.32	Į.		;	
0.011795	356.8	330.95	112.97			1 1	
0.022411	678.0	350 · C5	115.85			1 1	
0.044282	1888	873.8	119.82	16800	1.033	1.052	1 069
0.088465	2676	402.45	125.37	8490	1.101	1.091	1.103
0.14744	4460	426.6	130.89	5200	1.143	1.136	1.153
0.20642	6245	444.65	135.68	3720	1.189	1.180	1.218
0.29488	8921	466.1	142.54	2530	1.282	1.260	1.302
0.44232	13380	492.25	153.27	1620	1.411	1.408	1.445
0.58978	17840	512.5	165.17	1128	1.582	1.582	1.621
0 <i>-</i> 73721	22300	529·0	180.13	822	1.793	1.806	1.851
0.82568	24980	537.55	191.74	680	1.967	2.006	2.034
0.88465	26760	543.0	203.18	585	2.154	2.180	2.219
0.94363	28545	548 25	220.87	486	2.454	-	2.517
0.97313	29440	550.8	235.96	432	2.689	. — .	2.774
1.00000	30252	553·0	306.7	308.7	3.703	3.741*	8.827

By an error in copying, this number has been given as 3.710 in previous papers.
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Ratios	Absolute Temperature. Absolute critical temperature.		Volume of liquid. Critical volume.			Volume of saturated vapour. Critical volume.			
to critical pressures.	Hexa- methylene.	Benzene.	Normal hexane.	Hexa- methylene.	Benzene.	Normal hexane.	Hexa- methylene.	Benzene.	Normal hexane.
0.001474	0.5097	0.2088	0.5263	0.3466	0:3428]			
0.001474	0.5854	0.5359	0.5524	0.3526	0.3428	0.8494		-	, —
0.002848	0.5646	0.5648	0.5814	0.3527	0.3560	0.3563			_
0.011795	0.5985	0.5989	0.6144	0.8684	0.3648	0.3649			
0.022411	0.6330	0.6384	0.6489	0.3777	0.8742	0.3746		l —	_
0.044232	0.6759	0.6765	0.6907	0.3907	0.3870		54.8	54.4	55.9
0.088465	0.7277	0.7282	0.7406	0.4088	0.4053	0.4058	27.7	28-2	29.1
0.14744	0.7714	0.7725	0.7831	0.4268	0.4233	0.4234	17.0	17.25	17.6
0.20642	0.8041	0.8052	0.8145	0.4424	0.4389	0.4898	12.1	12.35	12.4
0.29488	0.8428	0.8429	0.8504	0 4648	0.4602	0.4611	8.25	8.49	8.48
0.44282	0.8901	0.8906	0.8955	0.4997	0.4960	0.4964	5 28	5.85	5.36
0.58978	0.9267	0.9270	0.8808	0.2382		0.5357	3.68	8.72	3.78
0.73721	0.9566	0.9566	0.9591	0.5873	0.5845	0.5851	2.68	2.69	2.69
0.82568	0.9720	0.9725	0.9740	0.6252	0.6250	0.6258	2.22	2.20	2.22
0.88465	0.9819 0.9914	0.9824	0.9833 0.9922	0.6625	0.6618	0.6612	1.91	1.91	1.92
0.94868 0.97818	0.9960	0.9915	0.9922	0·7201 0·7693	0.7113	0·7184 0·7706	1.59	_	1.60
1.00000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.41	1.00	1·41 1·00
1 00000	. 0000	2 0000	- 0000	1 0000	1 0000	1 0000	1 00	1 00	1 00

It will be seen that the temperature ratios of hexamethylene and benzene are almost identical, those of benzene being slightly higher (maximum difference 0.0011, minimum 0.0000, mean 0.0004). The ratios for normal hexane are, however, considerably higher (maximum difference 0.0170).

As a general rule, the volume ratios for the liquid state, except near the critical point where the change of curvature is very rapid and the liability to error correspondingly great, differ much less than the temperature ratios, so that the close agreement in this respect between benzene and normal hexane is not really so significant as that just referred to between hexamethylene and benzene. It is, however, worthy of remark that the ratios for hexamethylene are higher than those for any other "normal" substance yet investigated (Report Brit. Assoc., 1898, 831) except isopentane, the agreement in the case of these two hydrocarbons being, indeed, very close

As regards the ratios of the volumes of saturated vapour to the critical volumes, the values for benzene are, as a rule, intermediate between those for hexamethylene and for normal hexane; the differences are, however, but little greater than the probable errors of experiment.

Comparing the fifteen "normal" substances (data for two not yet published), it may be stated as a general law that if, for any substance, the temperature ratios are high, the ratios for the saturated vapour will also be high, and those for the liquid will be low, and vice versa. Hexamethylene forms no exception to this rule.

The most interesting comparison of the ratios of the actual to the theoretical densities of saturated vapour is at the critical point. Hexamethylene has a lower ratio than any of the other seven hydrocarbons, or, indeed, than any other substance in the "normal" group except carbon tetrachloride, and, if Amagat's results be included, carbon dioxide. The difference from the theoretical value 3.77 (Trans., 1897, '71, 452) is, however, less than 2 per cent.

In conclusion, we desire to tender our thanks to the Government Grant Committee of the Royal Society for assistance in carrying out this research.

University College, Bristol.

LXXXIV.—The Composition and Tensions of Dissociation of the Ammoniacal Chlorides of Cadmium.

By WILLIAM ROBERT LANG, D.Sc., and ALBERT RIGAUT.

THE phenomena of dissociation were first investigated by H. St. Claire Deville and by Debray (Compt. rend., 1867, 64, 603; 1868, 66, 134). Following on this, Isambert (Ann. de l'École Normale, 1868) carried out an exhaustive research on the tensions of dissociation of certain ammoniacal compounds of the metals, and, by applying the principles set forth in Debray's papers, was enabled to arrive at the true composition of these compounds. He shows that a definite chemical compound always has a constant tension of dissociation. Quite recently, Jarry (Thèse de la Faculté des Sciences de Paris, 1899) has applied the laws of dissociation in investigating ammoniacal compounds obtained with a solution of ammonia, and has established the fact that, for the ammoniacal halogen compounds of silver, formation and decomposition stop when the liquid saturating the compound is under a pressure equal to the tension of dissociation of the substance in vacuum. We have studied, from this point of view, the compounds formed between ammonia and cadmium chloride, using ammonia in the gaseous condition, in the liquid form, and in solution.

By the action of gaseous ammonia on dry cadmium chloride, Croft

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(Phil. Mag., [iii], 21, 355) obtained a dry powder, much heat being developed at the same time, and the mass increasing in bulk. To this compound he gave the formula CdCl₂,6NH₃. He also employed a solution of ammonia, and prepared a granular, crystalline substance corresponding with the formula CdCl₂,2NH₃. André (Compt. rend., 1887, 114, 908) also, employing a solution at 0°, formed a compound to which, as the result of one experiment, he gave the formula CdCl₂,5NH₃. We have followed the method of preparation indicated by him, and find that this compound is identical with that obtained by Croft.

Our procedure was as follows: three to four grams of cadmium chloride, rendered anhydrous by heating almost to the point of fusion, were placed in a tube with the neck drawn out, to allow of its being afterwards sealed at the blowpipe, and the whole immersed in solid carbonic anhydride. Dry gaseous ammonia was passed slowly into the tube, when the chloride increased in bulk largely, and, in about 2 hours, a layer of liquid ammonia had formed on the surface of the solid compound; the tube was sealed and left for 20 hours. It was found preferable to use the salt in small lumps, as, when in powder, the liquid failed to penetrate through the mass, even on standing for a month. The tube was then cooled to -70° and opened, the temperature cautiously raised to -30° by means of methylic chloride, and the liquid ammonia expelled. In some of our experiments we allowed the ammonia to evaporate at 0° . After this the tube was sealed at the blowpipe and weighed. Analysis gave:

	Calculated for CdCl ₂ ,6NH ₃ .	Found.
CdCl ₂	 64.21	64.02
NH_3	 35 ·8	36.00

After reopening and heating at 100° until no more ammonia was evolved, analysis gave, as the result of several determinations:

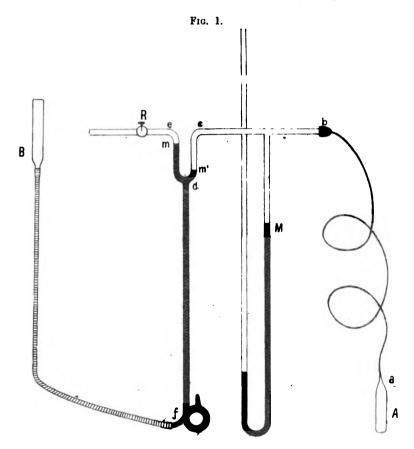
	Calculated for CdCl2,2NH2.	Found.
CdCl	 84.4	84.49
STITE -	 15.0	15.51

The formula of this compound is therefore CdCl₂, 2NH₃; it is inodorous, and, like the corresponding salt of zinc, only begins to
decompose at about 210°. At 360°, decomposition is still incomplete,
and when raised to close on 400° it fuses, giving only a trace of oxychloride and of chloride of ammonium.

In order to determine the tensions of dissociation of this hexammoniacal cadmium chloride, we used an apparatus similar to that of Jarry, and which is shown in Fig. 1.

A glass vessel, A a, containing the substances under consideration,

and in which the compound was prepared, is fixed by means of sealing wax to one of the extremities of a length of narrow lead tubing. The use of rubber should be avoided when working with gaseous ammonia, as the latter is readily dissolved by the rubber, and is given off again when the pressure is diminished. This tube is attached at b to the apparatus, which is mounted on a solid stand. The glass tube b c d e allows of communication being made with a mercury pump by means



of the stopcock R; the small U-tube c d e communicates by means of the vertical tube df with B, which contains mercury, and which can be lowered or raised at will. This allows of the tube c d s being filled with mercury, and so shutting off the vessel A, when a vacuum is produced, from the stopcock R. This is a very necessary precaution, as the gaseous ammonia dissolves in the grease with which this stopcock is lubricated. When a vacuum is maintained in the tube m, the

difference of levels at m and m' measures directly the pressure in A. As the tube m m' is only some 30 cm. high, higher pressure can be read on the tube M, which is open to the air, and stands about 2 metres high.

The numbers we obtained are:

Temp.	Press.	Temp.	Press.
0° ¯	46 mm.	50°	455 mm.
13	68	52	511
22	133	59	631
25	152	60	696
31	181	61	711
39	235	63	776
44	290	65	831
48	411	69	931

The readings were made in the following manner: The temperature of the water-bath in which the vessel A was immersed was very gradually raised, and the lamp removed; the thermometer fell slowly, and the mercury in the manometer rose, and, when it appeared to have attained a maximum, the readings were taken, at the same instant the temperature in the water-bath being noted.

It will be seen that above 62° the substance CdCl₂,6NH₃ can no longer exist, whilst we have at 100° a very stable compound, CdCl₂,2NH₃. It must therefore be at temperatures between 62° and 100° that the intermediate products are obtained.

We prepared this ammoniacal compound in the wet way also. By moistening hydrated cadmium chloride with a 20 per cent. solution of ammonia until thoroughly saturated, the compound is formed, increase in bulk taking place and much heat being developed. The crystals so obtained were dried over lime, and found to correspond with the formula CdCl₂,2NH₃. If a solution of cadmium chloride in aqueous ammonia is evaporated over lime, or if the crystals formed when this solution is heated to 50° are collected, the same compound is in every case obtained.

In order to obtain a compound containing more than 2 molecules of NH₈ by means of aqueous ammonia, it is necessary to pass a current of gaseous ammonia into a solution of cadmium chloride in a 20 per cent. solution of ammonia, keeping the temperature at 0°. An abundant precipitate is thus got of small, transparent crystals, which, when dried and pressed between filter paper, become opaque, losing ammonia. André (loc. cit.) also prepared those crystals, and, as mentioned elsewhere, gave them the formula CdCl₂,5NH₈. From an analysis of them, we are led to the conclusion that the formula is not CdCl₂,5NH₈, but that it is as indicated by

Croft (loc. cit.), namely, CdCl₂,6NH₈. This confirms Jarry's conclusions regarding the ammoniacal compounds of silver (loc. cit.). We have, besides, determined the tension of dissociation of this compound. At 22°, we found it to have a tension of 147 mm. instead of 135 mm. The excess obtained from this product is due to a small quantity of vapour of water, difficult to completely remove by pressing with bibulous paper.

From these experiments, it appears to us that it is possible to obtain the same ammoniacal compounds, either by the use of gaseous ammonia or from a sufficiently concentrated solution.

A short note, containing a portion of the results here set forth, has been communicated to the Académie des Sciences, Paris, by Prof. Troost, of The Sorbonne, to whom we desire to tender our best thanks for his kind assistance and advice.

CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW, August, 1899.

LXXXV.—The Aluminium-Mercury Couple. Part I.
Action of Sulphur Chloride on some Hydrocarbons
in presence of the Couple.

By Julius Berend Cohen and Frederick William Skirrow, The Yorkshire College.

It has been shown by Hirst and Cohen (Trans., 1895, 67, 826) that the action of the aluminium-mercury couple closely resembles that of aluminium chloride, investigated by Friedel and Crafts, in bringing about combinations between certain halogen compounds and the aromatic hydrocarbons.

We have continued the investigation into the action of the couple in other directions, and find that, like aluminium chloride, it is capable of very general application as a condensing agent and also as a halogen carrier. The advantage of using the couple consists in the ease with which it is prepared and in the fact that, the action being apparently a contact action, a very minute quantity of the couple suffices for the preparation of a considerable quantity of material.

If a few drops of sulphur chloride (S₂Cl₂) are added to a little benzene and a small fragment of the couple dropped in, a violent reaction ensues. The liquid boils and the colour rapidly darkens whilst large volumes of hydrogen chloride gas are evolved.

As the same vigorous action occurs with the majority of aromatic hydrocarbons investigated, it is necessary to moderate it by using

an excess of the hydrocarbon and by adding the sulphur chloride gradually. Another point of importance is the employment of the couple in a freshly-prepared state. The couple, when kept for a short time even out of contact with the air, appears to lose its active property, and fails to produce any immediate action. On the other hand, metallic aluminium alone will react after some time; but in this case the action appears to depend on the formation of aluminium chloride, for the metal gradually dissolves.

The chief product of the action described above is diphenylene disulphide and its homologues, the principal action taking place according to the following equation,

$$2C_6H_6 + S_2Cl_2 = C_6H_4 < S > C_6H_4 + 2HCl.$$

Compounds of this character were only isolated in a pure state from benzene and toluene. In the case of the other hydrocarbons, yellow oils were obtained, which it was found impossible to purify, since they decompose on distillation. At the same time, the interesting observation was made that, on distillation in a vacuum, these substances yield the sulphhydrate or thiophenol of the hydrocarbon in the form of either well crystallised solids or low boiling liquids, which may be prepared in a pure state.

Diphenylene Disulphide,
$$C_6H_4 < S > C_6H_4$$
.

This substance was obtained by Friedel and Crafts (Ann. chim. phys., 1884, [vi], 1, 530), along with phenylic sulphide, by the action of sulphur chloride in presence of aluminium chloride, and also from benzene, sulphur, and aluminium chloride (Ann. chim. phys., 1888, [vi], 14, 438).

The present method of preparation is as follows: 60 grams of benzene are placed in a flask attached to an upright condenser, and about 0.5 gram of the couple is then added. The couple is obtained, as previously described (Trans., 1895, 67, 826), by placing aluminiumfoil in mercuric chloride solution; it is then well washed with water, alcohol, and finally ether, and dropped into the flask. A bent tube attached to the upper end of the condenser and dipping under caustic soda solution absorbs the fumes of hydrochloric acid which are evolved. Twenty grams of sulphur chloride are now added in portions of about 2 c.c. at a time. The first addition of the chloride produces a curious change in the appearance of the couple; black spots appear on the metal, and as the action proceeds the deposit covers the whole surface; subsequently, some of the black deposit becomes detached, and adheres to the bottom of the vessel. When

the first brisk evolution of gas begins, the liquid becomes hot, and the colour changes to brown, and finally to a deep blue. The sulphur chloride being all added, the flask is heated for a short time on the water-bath to complete the action, and the contents allowed to cool. A quantity of sulphur is deposited on cooling; the liquid is then decanted into a separating funnel, the residue in the flask washed with benzene or ether, and the washings added to the decanted portion. Although the weight of the couple employed is exceedingly small, in no case was there any appreciable diminution in quantity at the end of the process, and it is apparently unattacked.

The liquid in the separating funnel is well shaken up with water to remove hydrochloric acid, and to decompose unchanged sulphur chloride. The colour of the liquid changes to light orange. separated and dehydrated over calcium chloride and the ether or benzene distilled off on the water-bath. The residue, on cooling, forms a mass of crystals weighing about 16 grams, impregnated with an orange-coloured oil. The oil is removed by draining on a porous plate, which entails a considerable loss of the solid product, as only about half the weight of the crystalline compound remains. By afterwards extracting the porous plate with ether and distilling off the ether, a residue is left which becomes semi-solid on standing, and from this a further quantity of crystals may be obtained. An attempt was made to determine the character of the oil, but it was impossible to free it entirely from the solid. The crude diphenylene disulphide was purified by crystallisation from alcohol and then forms colourless, crystalline needles melting at 148° (Friedel and Crafts give 149°). dissolves in concentrated sulphuric acid with a deep purple colour and is reprecipitated unchanged by water. It is therefore identical with Friedel and Crafts' compound, and its identity was confirmed by the following analysis:

0.1515 gave 0.3280 BaSO₄. S = 29.7. (C₆H₄S)₂ requires S = 29.6 per cent.

Diphenylene Disulphone, $C_6H_4 < SO_2 > C_6H_4$.

This compound, which was originally obtained by Friedel and Crafts by oxidising the disulphide with chromic acid in glacial acetic acid, is more readily prepared by simply digesting it with strong nitric acid, when a quantitative yield is obtained.

One gram of the disulphide was added to 5 c.c. of strong nitricacid, in which it dissolved on warming; 5 c.c. of fuming nitric acid were then added, and the whole evaporated down on the water-bath; another 5 c.c. of fuming acid were added, and the solution again evaporated to

dryness. A crystalline mass weighing 1.3 grams remained, which was washed with water and recrystallised from glacial acetic acid. It forms glistening, white prisms, which melt above 300°.

0.0787 gave 0.1305 BaSO₄.
$$S = 22.7$$
. $(C_6H_4SO_2)_2$ requires $S = 22.9$ per cent.

$$\textit{Ditoluylene Disulphide}, \text{CH}_{\text{3}}\text{-}\text{C}_{\text{6}}\text{H}_{\text{3}}\text{-}\text{C}_{\text{6}}\text{H}_{\text{3}}\text{-}\text{CH}_{\text{8}}.$$

The substance was prepared by the method used in the case of the benzene compound, and was subsequently distilled under diminished pressure. Although Jacobson and Ney (Ber., 1889, 22, 911) describe the substance obtained by them from toluylene diazosulphide as a crystalline compound melting at 116°, the product which we obtained, although it boiled constantly at 230—235° under 60 mm. pressure, showed no sign of crystallisation. Like the benzene compound, it dissolved in strong sulphuric acid with a deep blue colour, and gave the following result on analysis:

0.2482 gave 0.4799 BaSO₄.
$$S = 26.5$$
. $(C_7H_6S)_2$ requires $S = 26.2$ per cent.

From experience with the higher homologues, it was thought possible to split up the molecule by heating it at atmospheric pressure; but at a temperature of 360° it remained entirely unchanged, afterwards distilling at 226—233° at 50 mm. It is oxidised by means of fuming nitric acid to

Ditoluylene Disulphone,
$$CH_3 \cdot C_6H_3 < SO_2 > C_6H_3 \cdot CH_3$$
.

The substance crystallises from glacial acetic acid in colourless needles, the yield being quantitative.

0.1843 gave 0.2867 BaSO₄.
$$S = 21.1$$
. $(CH_3 \cdot C_6H_8 \cdot SO_9)_9$ requires $S = 20.8$ per cent.

Action of Sulphur Chloride on Metaxylene.

In this case, a large quantity of light brown, rather viscid, oil was obtained, which did not crystallise. We attempted to purify it by distillation in a vacuum, but on heating it under a pressure of 40 mm. it decomposed when the temperature reached 200°, and a mobile, pale yellow liquid distilled. It was redistilled under 60 mm. pressure and boiled at 92—100°; it was analysed with the following result:

I. 0.1996 gave 0.3370 BaSO₄. S = 23.2.

II. 0.1685 , 0.2700 BaSO_4 . S = 23.0.

 $C_6H_4(CH_8)_2S$ requires $S=23\cdot2$ per cent

Although the analysis agrees very closely with that of dixylylene disulphide, the low boiling point led us to suspect that the original compound had decomposed into xylyl sulphhydrate or thioxylenol $C_6H_8(CH_8)_2$ ·SH. We were able to confirm this view, for the substance gave a colourless, crystalline precipitate with an alcoholic solution of mercuric chloride characteristic of mercaptans, and its molecular weight determined by the cryoscopic method in benzene agreed with the formula of the sulphhydrate.

Weight of benzene, 10.747 grams; weight of substance, 0.0615 gram. Lowering of the freezing point, 0.208°.

 $\begin{aligned} & \textbf{Molecular Weight} = 134 \cdot 8. \\ & \textbf{Calculated for C}_6 \textbf{H}_4 (\textbf{CH}_3)_2 \textbf{S}: \ \textbf{M.W.} = 138. \end{aligned}$

It has a peculiar but by no means disagreeable smell. On oxidation with nitric acid, a solid substance was obtained crystallising in needles, but it was not investigated.

The thioxylenol, which was obtained by Yssel (Zeit. f. Chem., 1865, [ii], 1, 360) by the action of zinc and sulphuric acid on xylene-sulphonic chloride, is described as a liquid boiling at 213°.

Action of Sulphur Chloride on Cumene.

The action is similar to that on xylene. A quantity of orange-coloured oil was obtained, consisting probably of dicumylene disulphide, but it was impossible to purify it. On distillation under diminished pressure, it decomposed, leaving a tarry residue in the distilling flask; the distillate, which came over below 200°, had an amber colour, and solidified on cooling. Four grams of distillate were obtained from 10 grams of sulphur chloride originally employed. The substance was drained on a porous plate to remove adhering oil, and then recrystallised from alcohol, from which it separates in large, colourless plates melting at 87—90°.

0.1327 gave 0.2085 BaSO₄. S = 21.2. $C_9H_{12}S$ requires S = 21.05 per cent.

This substance, like the xylene compound, has half the molecular weight of the disulphide. Two determinations gave the following result:

- I. Weight of benzene, 8.76 grams; weight of substance, 0.122 gram. Lowering of the freezing point, 0.494°.
- II. Weight of benzene, 8.76 grams; weight of substance, 0.0892 gram. Lowering of the freezing point, 0.322°.

Molecular weight (I) = 140; (II) = 158.

Calculated for $C_0H_{19}S: M.W. = 152$.

With an alcoholic solution of mercuric chloride, it gives a compound crystallising in needles, which is apparently, not cumyl sulphhydrate, but is probably identical with the pseudocumyl compound described by Beilstein and Kögler (*Annalen*, 1866, 137, 322), which corresponds closely with it in crystalline character and melting point (86—87°).

The formation of this compound is unaccountable, unless the hydrocarbon (obtained from Kahlbaum) contained a very large proportion of pseudocumene, which is scarcely probable, and we are at present unable to explain the formation except as the result of intramolecular change.

Action of Sulphur Chloride on Pseudocumene.

The action in the case of pseudocumene was very vigorous, and on distilling the resulting oil in a vacuum, a light yellow liquid passed over below 200° which completely solidified on cooling. Nine grams of solid distillate were obtained from 13 grams of sulphur chloride. The product was recrystallised from alcohol, when the less soluble portion which first crystallised formed large, tabular crystals, closely resembling the substance obtained from cumene. The identity of the two compounds was established by the melting point 87—90° and by analysis.

0.1191 gave 0.1815 BaSO₄. S = 20.9. $C_0H_{10}S$ requires S = 21.05 per cent.

The second product crystallises from the mother liquor in colourless needles melting at 110—111°, and is apparently the sulphide $[C_6H_2(CH_3)_8]_2S$.

Two different preparations gave the following results on analysis:

I. 0.0682 gave 0.060 BaSO₄. S = 12.08. II. 0.1002 , 0.0887 BaSO₄. S = 12.1.

 $C_{18}H_{22}S$ requires S=11.8 per cent.

Action of Sulphur Chloride on Cymene.

The action proceeded slowly at the ordinary temperature, but vigorously on warming; on distilling the product in a vacuum, a considerable quantity of the oil decomposed, leaving a tarry residue. The distillate boiled below 200° under a pressure of 35 mm., and was fractionated, the portions boiling at 120—130° and 130—150° being collected separately and analysed. Neither fraction was pure, but consisted probably of a mixture of the sulphide and sulphhydrate.

The first portion contained 11 per cent. of sulphur, and the second 16.4 per cent., whereas the calculated percentage of sulphur in the sulphide is 10.7 per cent., and in the sulphhydrate 19.2 per cent.

Action of Sulphur Chloride on Heptane.

Finally, the same reaction was tried with the fraction of petroleum spirit boiling at 95—100°, which consists mainly of heptane. The action of sulphur chloride in presence of the couple was very vigorous, and hydrochloric acid was evolved. A dark brown, amorphous powder was obtained mixed with sulphur; the brown compound dissolves in strong sulphuric acid, and is reprecipitated by water; but all attempts to crystallise it were unsuccessful.

LXXXVI.—The Aluminium-Mercury Couple. Part II.

The Action of Bromine on Organic Compounds in presence of the Couple.

By Julius B. Cohen and Henry D. Dakin, The Yorkshire College.

THE action of certain substances, such as iodine, metals and their salts, as bromine carriers, is well known and fully described in the "Laboratory Methods" of Lassar-Cohn, under the heading of "Bromine Carriers" (Bromüberträger). Among the substances enumerated are aluminium chloride and bromide. Metallic aluminium has also been used in one or two isolated cases (Blümlein, Ber., 1884, 17, 2486; Ris, Ber., 1887, 20, 2621; Gustavson, Beilstein's Org. Chem., 3rd. ed., I., 67), but as the aluminium in these cases is added to the bromine previously to introducing the organic compound, it is to be assumed that it is only a modification of the use of aluminium bromide, since aluminium and bromine would immediately react to form the bromide of the metal.

The activity of the aluminium-mercury couple in effecting combination between certain halogen compounds and the hydrocarbons suggested its application as a halogen carrier.

The following experiments show that it may be conveniently used for this purpose. The substances selected do not combine with bromine readily under ordinary conditions, but are rapidly brominated in presence of the couple. That the action is due mainly to the

couple, and not to any aluminium bromide which might be formed, is clearly indicated by the fact that the couple is scarcely attacked during the progress of the reaction.

The method is carried out as follows. A round flask to hold the hydrocarbon, or other substance, and the couple is attached to an upright condenser, the upper end of which is closed by a cork perforated with two holes. Through one of these a tap funnel for delivering the bromine is inserted, and through the other a bent tube passes, the long limb of which dips under water and absorbs the hydrobromic acid evolved. The product of the reaction is purified in the usual way.

Bromobenzene.—Fifty grams of benzene were taken, and about 0.5 gram of the couple added; sixty grams of bromine were then dropped in slowly from the tap funnel. The action proceeds vigorously, the liquid becomes warm, and volumes of hydrobromic acid are evolved. When in the course of about half an hour all the bromine has been added, the contents of the flask are shaken up with dilute caustic soda solution, the liquid dried over calcium chloride and fractionated.

Two experiments gave the following results on the first distillation:

"

I. 30 grams boiling at 140—170° (bromobenzene)

6 ,, ,, above 170°
II. 37 ,, ,, at 140—170°
5 ,, ,, above 170°

The two higher boiling fractions were mixed and distilled, and 5 grams boiling at 150—200° were obtained. The residue did not solidify on cooling, and consequently very little dibromobenzene was present. Calculated on the bromine taken, the yield is about 60 per cent. of the theoretical amount.

Bromotoluene.—Fifty grams of toluene and 60 grams of bromine yielded, on the first distillation:

The yield is about 50 per cent. of the theoretical quantity, which would no doubt be increased by further fractionation. The product is probably a mixture of the ortho- and para-compounds.

Parabromometaxylene.—Fifty grams of metaxylene and 60 grams of bromine gave, on the first distillation:

32 grams boiling at 185—210° (bromoxylene)
11 ,, ,, ,, 210—230°
5—6 ,, ,, above 230°

Parabromochlorobenzene.—Chlorobenzene reacts vigorously with bromine in presence of the couple, and yields bromochlorobenzene melting at $62-63^{\circ}$. On recrystallising from alcohol, it melted at $65-67^{\circ}$ (Beilstein gives $67\cdot4^{\circ}$).

Bromoparachlorotoluene.—Twenty-five grams of parachlorotoluene (from paratoluidine) and 30 grams of bromine gave a bromine derivative which decomposed when distilled at atmospheric pressure. At 40 mm., it distilled as follows:

The larger fraction was redistilled, and after about 2 c.c. had passed over, it boiled steadily at 130—135°. The analysis gave the following results:

0.244 gave 0.3862 AgCl + AgBr. $CH_{\circ} \cdot C_{\alpha}H_{\circ} ClBr$ requires AgCl + AgBr = 0.3947 gram.

Action of Bromine on Monobromobenzene.

The action of bromine on benzene previously described as yielding monobromobenzene, occurred in presence of an excess of benzene, and it was therefore interesting to find whether the action of the couple could effect further substitution.

Monobromobenzene was therefore treated with a further quantity of bromine. The action was apparently as vigorous as in the case of benzene, and the chief product was paradibromobenzene m. p. 87°. In the same way, paradibromobenzene was converted into tetrabromobenzene, m. p. 175—176° (the melting point of 1:2:4:5-tetrabromobenzene is given in Beilstein as 175°). With a large excess of bromine acting on the dibromobenzene, hexabromobenzene was formed. It was recrystallised from toluene, and gave the following result on analysis:

0.1520 gave 0.3060 AgBr. Br = 85.6. C_6 Br₆ requires Br = 86.9 per cent.

Action of Bromine on Bromoparachlorotoluene.

In presence of the couple, bromine acts vigorously on bromochlorotoluene, forming dibromochlorotoluene, m. p. 94°.

0.2135 gave 0.3925 AgCl + AgBr. $CH_3 \cdot C_6H_2ClBr_2$ requires AgCl + AgBr = 0.3898 gram.

Action of Bromine on Heptane.

Seventy-five grams of impure heptane from light petroleum boiling at 95—100° and 60 grams of bromine were allowed to react in presence of the couple in the manner described; the bromine was rapidly absorbed and hydrobromic acid evolved. After distilling off the unchanged light petroleum at the ordinary pressure, the remainder was fractionated at 100 mm.

A liquid boiling at 110—120° first distilled, which is probably heptylic bromide. At this point, the distillation was stopped and the contents of the flask poured out; the liquid, on cooling, formed a mass of colourless needles having a strong camphor-like odour. The crystalline mass was separated from adhering oil by spreading on a porous plate. It consisted of two substances, which could be easily separated by means of alcohol; the compound soluble in alcohol after recrystallisation melted at 88—90°, and gave the following result on analysis:

0.1285 gave 0.2324 AgBr. Br = 76.9. $C_7H_{12}Br_4$ requires Br = 76.9 per cent.

The substance is therefore a tetrabromoheptane.

The second product, which is only slightly soluble in alcohol, was recrystallised from glacial acetic acid. It forms colourless needles which did not melt at 250°, but on heating on platinum foil it fused and volatilised completely without decomposition, giving off a vapour having a strong odour of musk. It was analysed with the following result:

0.1327 gave 0.2379 Ag Br. Br = 76.2 per cent.

It therefore contains the same amount of bromine as the previous compound, which it accompanies; from its high melting point, it may possibly be polymeric with it.

The above account is a preliminary notice, and we propose to extend the investigation, especially into the action of bromine on the paraffins, and to prepare, if possible, their higher bromine derivatives, a group of compounds which are little known.

LXXXVII.—Experiments on the Constitution of Isocamphoronic Acid.

By WILLIAM HENRY PERKIN, jun., and Jocelyn Field Thorpe.

ISOCAMPHORONIC acid, $C_9H_{14}O_6$, appears to have first been described by Kachler in 1878 (*Annalen*, 191, 149), who prepared it, in the first instance, by the oxidation of camphor with nitric acid, and named it hydroxycamphoronic acid.

In 1879, Ballo (Ber., 12, 1597) oxidised camphor with chromic acid and obtained an acid which he believed to be adipic acid, but this Kachler soon afterwards (Ber., 1880, 13, 487) showed to be identical with his hydroxycamphoronic acid.

At a later date, Kachler (Monatch., 1883, 4, 648) found that considerable quantities of the same acid are produced when "oxycamphor" is oxidised with nitric acid.

The next important contributions to the subject were published by Tiemann (Ber., 1895, 28, 1344; 1896, 29, 2613) who showed that isocamphoronic acid is formed from pinonic acid—a product of the oxidation of pinene—and also from a campholenic acid—an acid closely allied to, and which may easily be converted into, pinonic acid—by oxidation with chromic acid mixture, isoketocamphoric acid being an intermediate product.

Tiemann is of opinion that the constitutions of these various substances may be represented by the formulæ,

and considers this view of the constitution of isocamphoronic acid is proved, because this acid when heated with concentrated sulphuric acid VOL. LXXV.

at 100° , is decomposed, with evolution of carbonic oxide and formation of terpenylic acid,

$$(\mathrm{CH_3})_2\mathrm{C}\text{--}\mathrm{CH}\text{--}\mathrm{CH_2}$$

Again, isocamphoronic acid, on oxidation, yields dimethyltricarballylic acid,

the formation of which is readily understood if Tiemann's formula is assumed to be correct.

Baeyer, on the other hand, as the result of his researches on the constitution of pinene, comes to quite different conclusions with regard to the formulæ of this terpene and of its principal decomposition products. Assuming that Wagner's formula for pinene is correct,

he formulates the constitutions of pinonic acid, isoketocamphoric acid, and isocamphoronic acid thus:

Pinonic acid,
$$CH_8 \cdot CO \cdot CH \stackrel{C(CH_8)_2}{\hookrightarrow} OH \cdot CH_2 \cdot COOH$$
,

Isokstocamphoric acid, $CH_3 \cdot CO \cdot CH_2 \cdot C(CH_3)_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$.
Isocamphoronic acid, $COOH \cdot CH_2 \cdot C(CH_3)_2 \cdot CH(COOH) \cdot CH_2 \cdot COOH$.

Baeyer explains the formation of the two latter acids from pinonic acid by assuming that an intermediate substance,

$$\mathrm{CH_8 \cdot CO \cdot CH} \underbrace{\mathrm{CO}_{\mathrm{CO}}}_{\mathrm{CO}} \underbrace{\mathrm{CH} \cdot \mathrm{CH}_{2} \cdot \mathrm{COOH}}_{\mathrm{2}},$$

is first produced, which then, by hydrolysis, yields isoketocamphoric acid, and he is of opinion that the formation of terpenylic acid from isocamphoronic acid by heating with concentrated sulphuric acid at 100° cannot be taken as a proof of the correctness of Tiemann's formula for the latter acid, since such energetic treatment may have brought about intramolecular rearrangement.

From this short sketch, it will be seen that the determination of the constitution of isocamphoronic acid is a matter of great importance owing to its bearing on the constitution, not only of pinene, but also of camphor, and on this account we have been experimenting, during the last two years, with a view of preparing synthetically an acid of the formula suggested by Baeyer, but the problem is one of unusual difficulty. We have, however, at length obtained an acid which we believe to have this constitution, but which we find is not identical with isocamphoronic acid.

A short time ago (Trans., 1899, 75, 63), we succeeded in preparing $a\beta\beta$ -trimethylglutaric acid by the following series of reactions. Ethylic dimethylacrylate, $(CH_8)_2C:CH:COOC_2H_5$, was digested in alcoholic solution with the sodium derivative of ethylic cyanacetate, $CN:CHNa:COOC_2H_5$, when combination took place with formation of the sodium derivative of ethylic cyanodimethylglutarate,

$$\mathbf{COOC_2H_5} \cdot \mathbf{C(CN)Na \cdot C(CH_8)_2} \cdot \mathbf{CH_2} \cdot \mathbf{COOC_2H_5}.$$

This, on treatment with methylic iodide, yielded ethylic cyanotrimethylglutarate, $COOC_2H_5$ · $C(CN)(CH_8)$ · $C(CH_8)_2$ · CH_2 · $COOC_2H_5$, from which by boiling with dilute sulphuic acid, $\alpha\beta\beta$ -trimethylglutaric acid, COOH· $CH(CH_8)$ · $C(CH_8)_2$ · CH_2 ·COOH, was obtained. We now find that, if the sodium derivative of ethylic cyanodimethylglutarate, instead of being treated with methylic iodide, is digested with ethylic bromacetate, the following reaction takes place:

The sthylic cyanodimethylbutanetricarboxylate thus produced—a colourless oil boiling at 223—227° under 25 mm. pressure—yields, on hydrolysis with dilute sulphuric acid, dimethylbutanetricarboxylic acid,

an acid which, it will be seen, has the same formula as that suggested by Baeyer for isocamphoronic acid. The synthetical acid obtained by us has the very remarkable property of being apparently incapable of crystallising. When isolated from the product of hydrolysis of ethylic cyanodimethylbutanetricarboxylate by extraction with ether in the usual way, it remains, after evaporating off the ether, as a thick, colourless syrup, which, on standing over sulphuric acid in a vacuum desiccator, froths up owing to the escape of ether, and is converted into a resin very similar to colophony in appearance. As it seemed possible that the acid did not crystallise because it was not quite

Digitized by G205 C

pure, a large quantity was reconverted into the triethylic salt, and this, on fractionation, was easily obtained pure as a colourless oil boiling quite constantly at 182—183° under 22 mm., and at 300—302° under 740 mm. pressure, the latter temperature coinciding exactly with the boiling point of the ethylic salt of camphoronic acid.

This ethereal salt, which gave correct numbers on analysis, was carefully hydrolysed, but the acid was again obtained as a resin which showed no signs of crystallising. As the acid yields a calcium salt which is much less soluble in hot than in cold water, a given quantity was separated into five fractions of calcium salts, but these each and all yielded a non-crystallisable acid. Again all attempts to convert the acid into crystalline derivatives, such as the amide, anilide, phenylhydrazide, &c., were unsuccessful. It, however, yields a crystalline strychnine salt, but on decomposing this, the acid was again obtained with the same resinous properties. If the acid is dissolved in acetone, and the solution mixed with benzene and allowed to stand for some weeks, crystals slowly separate which consist of dimethylbutanetricarboxylic acid combined with benzene; these very readily lose benzene, leaving as a residue the same resinous acid. are therefore forced to the conclusion that this dimethylbutanetricarboxylic acid is incapable of crystallising.

When dimethylbutanetricarboxylic acid is heated in a retort under diminished pressure, it readily loses water, and on distilling the residue, anhydrodimethylbutanetricarboxylic acid,

$$CH_2$$
— $CH \cdot C(CH_3)_2 \cdot CH_2$
 $CO \cdot O \cdot CO$ $COOH'$

passes over constantly at $240-242^{\circ}$ under 16 mm. pressure as a thick oil which shows no sign of crystallising, and which, when treated with aniline, β -naphthylamine, &c., gives only resinous derivatives.

Experiments are in progress with the view of preparing synthetically the acid of the formula which Tiemann assigns to isocamphoronic acid, and it is hoped that in this way the constitution of this important acid may soon be definitely established.

EXPERIMENTAL.

In order to prepare this substance, sodium (5 grams) is dissolved in absolute alcohol (70 grams), the solution mixed with ethylic cyanacetate (25 grams), and ethylic dimethylacrylate (28 grams)

and the whole heated for 2 days in a reflux apparatus on the water-bath. The white, crystalline sodium compound of ethylic cyanacetate which at first separates, gradually dissolves, and in about 4 hours a light brown liquid is formed. At the end of two days, the product has become converted into a hard, brown mass of the sodium compound of ethylic cyanodimethylglutarate,

 ${\rm COOC_2H_5 \cdot C(CN)Na \cdot C(CH_8)_2 \cdot CH_2 \cdot COOC_2H_5}.$

To this, after cooling, ethylic bromacetate (40 grams) is added, and the heating continued, when sodium bromide rapidly separates, and after 6 hours the brown sodium compound is entirely decomposed. The product, which should be quite neutral, is mixed with water and extracted with ether; the ethereal solution is washed well with water, dried over calcium chloride and evaporated, and the residual oil, which weighs about 70 grams, submitted to very careful fractional distillation under reduced pressure (25 mm.). In this way, after four or five fractionations, two principal fractions are obtained boiling respectively at $180-200^{\circ}$ and $220-230^{\circ}$. The first of these consists of ethylic cyanodimethylglutarate (Trans., 1899, 75, 52), which has escaped interaction with the ethylic bromacetate; the higher fraction yields, on further distillation, a thick, colourless oil, which boils constantly at about $223-227^{\circ}$, under 25 mm. pressure, and consists of *ethylic cyanodimethylbutanetricarboxylate*.

The yield of this cyano-ethereal salt from the quantities given above is about 35 grams.

Dimethylbutanetricarboxylic Acid, COOH·CH₂·CH(COOH)·C(CH₂)₂·CH₂·COOH.

This acid is readily obtained by the hydrolysis of ethylic cyanodimethylbutanetricarboxylate, as explained in the introduction to this paper. The pure ethereal salt (10 grams) is mixed with 40 per cent. sulphuric acid (about 50 grams) and the whole heated to boiling in a reflux apparatus for two days, when the ethereal salt rapidly passes into solution with evolution of carbon dioxide and alcohol, the latter being allowed to escape by removing the condenser from time to time for a few minutes. The product is saturated with ammonium sulphate and extracted four times with pure ether, when practically the whole of the acid will have passed into the ether, the ease with which this extraction takes place being somewhat remarkable. The ethereal

solution, after drying over calcium chloride and evaporating, deposits a thick, gummy mass, which apparently consists of nearly pure dimethylbutanetricarboxylic acid, but as all attempts to obtain this acid in a crystalline condition were unsuccessful, it was next converted into its ethylic salt and this subjected to very careful purification. The acid (120 grams) was dissolved in absolute alcohol (500 grams), the solution mixed with one-fifth of its volume of concentrated sulphuric acid, and allowed to stand for 2 days. Water was then added and the ethylic salt extracted four times with ether; the ethereal solution was washed well with water and dilute sodium carbonate, dried over anhydrous potassium carbonate and evaporated, when 87 grams of an almost colourless oil remained. On acidifying the sodium carbonate washings and extracting with ether, 64 grams of an acid ethylic salt were obtained, which was again etherified by treatment with alcohol and sulphuric acid.

The combined ethylic salts were then most carefully fractionated under reduced pressure, and after three distillations, about two-thirds of the whole quantity was obtained as a colourless oil, which distilled constantly at 182—183° under a pressure of about 22 mm., and almost without decomposition at 303—305° under the ordinary pressure.

This oil, on analysis, gave numbers agreeing closely with those required for sthylic dimethylbutanetricarboxylate.

```
0.2026 gave 0.4421 CO<sub>2</sub> and 0.1580 H<sub>2</sub>O. C=59.52; H=8.66. 0.1824 ,, 0.399 CO<sub>2</sub> ,, 0.1415 H<sub>2</sub>O. C=59.60; H=8.62. C_{15}H_{26}O_6 requires C=59.60; H=8.61 per cent.
```

Hydrolysis.—It has been stated in the introduction to this paper that the hydrolysis of pure ethylic dimethylbutanetricarboxylate yielded a resinous acid; the experiment was conducted as follows: The pure ethylic salt (5 grams) was boiled with methyl alcoholic potash (5 grams) for 4 hours, when, on standing, a solid potassium salt separated; this was collected, washed with a little methylic alcohol, dissolved in water and evaporated until quite free from alcohol. solution was acidified, saturated with ammonium sulphate and extracted four times with pure ether; the ethereal solution was then dried over calcium chloride and evaporated, when a resinous acid was obtained which would not crystallise, even when a crystal of isocamphoronic acid (for a quantity of which acid I am indebted to Prof. Baeyer) was stirred up with it. When left in a vacuum desiccator, the acid frothed up and lost the ether remaining in it only with extreme difficulty. The alcoholic mother liquors of the above potassium salt were also mixed with water, evaporated, acidified, and extracted in the same way, and in this case again the acid remained resinous.

Dimethylbutanetricarboxylic acid, on analysis, gave the following numbers:

```
0.1251 gave 0.2300 CO<sub>2</sub> and 0.0785 H_2O. C = 50.14; H = 6.97. 0.1376 , 0.2520 CO<sub>2</sub> , 0.0847 H_2O. C = 49.95; H = 6.83. C_9H_{14}O_6 requires C = 49.54; H = 6.42 per cent.
```

The somewhat high numbers obtained are due to the fact that, owing to the resinous nature of the substance, it was impossible to remove the last traces of ether.

The silver salt, $C_9H_{11}O_6Ag_8$, was obtained by adding silver nitrate to a neutral solution of the ammonium salt as a white, amorphous precipitate, which, after well washing and drying, first over sulphuric acid and then at 100° , gave the following results on analysis:

```
0.251 gave 0.1835 CO<sub>2</sub>, 0.0453 H<sub>2</sub>O, and 0.1511 Ag. C = 19.79; H = 2.00; Ag = 60.15. 0.5686 gave 0.3427 Ag. Ag = 60.27.
```

 $C_9H_{11}Ag_8O_6$ requires $C=20\cdot04$; $H=2\cdot04$; $Ag=60\cdot11$ per cent.

A neutral solution of the ammonium salt shows the following behaviour with reagents. Calcium chloride gives no precipitate in the cold, but on boiling, a white, amorphous salt separates at once; this is readily soluble in cold, but only sparingly so in boiling water. Barium chloride and zinc chloride give no precipitates, even on boiling. When copper sulphate is gradually added to the neutral solution, the palegreen precipitate which first forms, dissolves in the excess of the ammonium salt, but on adding excess of copper sulphate, the copper salt is thrown down as an insoluble precipitate. Lead acetate shows a similar behaviour, yielding, with excess of the precipitant, a white, amorphous, insoluble lead salt.

Since the calcium salt is characteristic, being more soluble in cold than in hot water, it seemed possible that, by making use of this peculiarity, we might succeed in obtaining dimethylbutanetricarboxylic acid in a crystalline condition. The acid (20 grams) was therefore dissolved in an excess of ammonia, mixed with a strong solution of calcium chloride, the clear liquid heated to boiling, and when a considerable quantity of the calcium salt had separated, the whole was rapidly filtered by the aid of the pump, using a hot water funnel; the residue was washed with boiling water and spread on a porous plate. By concentrating and boiling the filtrate and repeating the above process, the 20 grams of acid were ultimately converted into 5 fractions of the calcium salt; these were separately dissolved in water, acidified with hydrochloric acid, and the acid extracted with ether in the usual way, but in all cases a resinous acid was obtained which did not show any signs of crystallising.

After experimenting with several other salts, the strychnine salt was at last prepared by adding powdered strychnine to a strong, warm, aqueous solution of the acid, when it was found that large quantities of the base were very readily dissolved. The solution gradually crystallised, and after standing for 3 weeks, the whole had become filled with ill-defined voluminous, nodular crystals; these were collected by the aid of a vacuum pump, rapidly washed with a little water, and spread on a porous plate. The salt was then dissolved in water, and the strychnine precipitated by means of potash; after filtering and acidifying the filtrate, the acid was extracted in the usual way, but in this case also it was again obtained in the form of a resin.

Anhydrodimethylbutanetricarboxylic Acid,
$$CH_2$$
— $CH \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH$. $CO \cdot O \cdot CO$

When pure dimethylbutanetricarboxylic acid is heated in a fractionation flask under reduced pressure (16 mm.), the mass at first froths owing to elimination of water, and the residue then distils completely between 235° and 250°; on refractionation almost the whole passes over between 240° and 242° under 16 mm. pressure as a pale yellow, very thick oil, which, on cooling, sets to an almost solid, transparent resin, and consists of pure anhydrodimethylbutanetricarboxylic acid, as the following analysis shows.

0.1992 gave 0.3926 CO₂ and 0.1069 H₂O. C=53.81; H=5.96.
$$C_9H_{12}O_5$$
 requires C=54.0; H=6.0 per cent.

This anhydro-acid dissolves readily in water, being evidently again converted into the tribasic acid.

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LXXXVIII.—The cis- and trans-β-Phenylbutane-aa₁a₂tricarboxylic Acids,

 $\mathbf{COOH} \boldsymbol{\cdot} \mathbf{CH_2} \boldsymbol{\cdot} \mathbf{CH}(\mathbf{C_6H_5}) \boldsymbol{\cdot} \mathbf{CH}(\mathbf{COOH}) \boldsymbol{\cdot} \mathbf{CH_2} \boldsymbol{\cdot} \mathbf{COOH}.$

By Jocelyn Field Thorpe and William Udall.

In the preceding paper, it was shown that $\beta\beta$ -dimethylbutane- $\alpha a_1 a_2$ -tricarboxylic acid not only differs considerably from isocamphoronic acid, to which Baeyer assigned this constitution, but also exhibits the remarkable property, not usually associated with tricarboxylic acids, that neither it nor its derivatives show any tendency to crystallise.

For the latter reason especially, it seemed to us that it would be interesting to prepare an analogously constituted acid and study its properties, and in doing this we selected for synthesis β -phenylbutane- aa_1a_2 -tricarboxylic acid, because this acid, containing as it does an aromatic group, might be expected to show a considerable tendency to crystallise. The method adopted in this synthesis was the following. In the first place, ethylic cinnamate was digested in alcoholic solution with the sodium compound of ethylic cyanacetate, when combination readily took place with the formation of the sodium compound of ethylic β -phenyl-a-cyanoglutarate,

$$\begin{aligned} \text{COOC}_2\mathbf{H}_5 \cdot \text{CH:CH} \cdot \text{C}_6\mathbf{H}_5 + \text{CN} \cdot \text{CH}(\mathbf{Na}) \cdot \text{COOC}_2\mathbf{H}_6 \\ &= \text{COOC}_2\mathbf{H}_5 \cdot \text{CH}_2 \cdot \text{CH}(\mathbf{C}_6\mathbf{H}_5) \cdot \text{C}(\mathbf{Na})(\text{CN}) \cdot \text{COOC}_2\mathbf{H}_5. \end{aligned}$$

This sodium compound reacts readily with ethylic bromacetate, yielding ethylic β-phonylbutane-a₁-cyano-aa₁a₂-tricarboxylate,

 $COOC_2H_5 \cdot CH_2 \cdot CH(C_6H_5) \cdot C(CN)(COOC_2H_5) \cdot CH_2 \cdot COOC_2H_5$, a thick oil, distilling with partial decomposition at 270—280° under 20 mm. pressure.

When this ethereal salt is hydrolysed first with alcoholic potash and then with hydrochloric acid, a syrupy acid results, which could only be obtained in a crystalline form by dissolving it in acetone, adding benzene, and allowing the mixture to stand for some days. The crystals which gradually separate, and which melt between 130—137°, were found on examination to consist of a mixture of the cis- and transmodifications of phenylbutanetricarboxylic acid, crystallising with half a mol: of benzene. When these crystals are boiled with much water they dissolve, and, on cooling, the trans-acid separates in well-defined prisms melting at 195° and containing $\frac{1}{2}H_2O$; the cis-modification, being much more soluble, remains in the mother liquors.

When the trans-acid is digested with acetyl chloride, it is readily converted into an anhydro-acid of the probable constitution,

$$\underbrace{\text{CO} \cdot \text{CH}_2}_{\text{CO}} \rightarrow \text{CH} \cdot \text{CH}(\text{C}_6\text{H}_5) \cdot \text{CH}_2 \cdot \text{COOH},$$

which crystallises in needles, melts at 134—135°, and when boiled with water dissolves with formation of the cis-modification.

This cis-acid melts at 178—180°, and differs from the trans-acid in being much more soluble in water, and in yielding a barium salt which is much less soluble in hot than in cold water; when digested with acetyl chloride, it is converted into the same anhydro-acid melting at 134—135° as that obtained under similar conditions from the transacid.

In many respects, there is a considerable similarity in the properties of the phenylbutanetricarboxylic acids and the dimethylbutanetricarboxylic acid described in the previous paper. trans-Phenylbutanetricarboxylic acid described in the previous paper.

tricarboxylic acid, which, as stated above, crystallises with $\frac{1}{2}H_2O$, cannot be obtained in an anhydrous condition by heating, because it passes into the anhydro-acid at the temperature at which dehydration takes place.

If a solution of the *trans*-acid in ether is dried over calcium chloride, the acid is obtained, on distilling off the ether, as a gum which refuses to crystallise, but which, in contact with water, readily passes into the hydrated crystalline form.

It would be interesting to determine whether other acids of similar constitution to these dimethyl- and phenyl-butanetricarboxylic acids would show the same indisposition to crystallise.

$$\label{eq:cooc_adj} \begin{split} &\textit{Ethylic β-Phonylbutane-a_1-cyano-aa_1a_2$-tricarboxylate,} \\ &\mathrm{COOC_2H_5}\cdot\mathrm{CH_2}\cdot\mathrm{CH(C_6H_5)}\cdot\mathrm{C(CN)(COOC_2H_5)}\cdot\mathrm{CH_2}\cdot\mathrm{COOC_2H_5}. \end{split}$$

In preparing this ethylic salt, $11\frac{1}{2}$ grams of sodium were dissolved in 140 grams of absolute alcohol, and after mixing with 65 grams of ethylic cyanacetate, 90 grams of ethylic cinnamate were added; the mixture was heated for 18 hours on the water-bath, 90 grams of ethylic bromacetate were then gradually added, and the whole heated until neutral. On extracting the product in the usual way, a thick, brownish oil was obtained, the greater portion of which, on fractionating under diminished pressure, distilled between 270° and 280° (20 mm.) as a thick yellow syrup.

0.2101 gave 0.4861 CO₂ and 0.1613 H₂O. C = 63.10; H = 6.31. $C_{20}H_{25}NO_6$ requires C = 63.32; H = 6.59 per cent.

Since, however, this ethylic salt decomposes to a large extent during the process of distillation, it is advisable not to submit it to fractionation, as this is not necessary in preparing the phenylbutanetricarboxylic acids; the simplest plan is to remove the products of lower boiling point by distillation in a current of steam, and then to hydrolyse the non-volatile oil by means of an equal weight of potassium hydroxide dissolved in methylic alcohol. After heating for two hours, the alcohol is removed by evaporation, the residue dissolved in water, acidified, filtered from the precipitate which is produced, and the filtrate, after saturating with ammonium sulphate, extracted repeatedly The distillation in steam removes the excess of ethylic cyanacetate, and the precipitate which is obtained on acidifying the product of hydrolysis consists of cinnamic acid together with a small quantity of β-phenylglutaric acid, COOH·CH₀·CH(C₆H₆)·CH₂·COOH, melting at 135° (Michael, J. pr. Chem., 1887, [ii], 35, 352). On evaporation, the ethereal extract of the filtrate deposited a resin which showed no tendency to crystallise, and in spite of the treatment

with alcoholic potash, still contained a large quantity of nitrogen. It was therefore further hydrolysed by boiling for 10 hours with concentrated hydrochloric acid, and the product after evaporation to dryness, was extracted in a Soxhlet apparatus with ether. On evaporating the ether, a gum remained, which, when dissolved in acctone and mixed with five times its volume of benzene, slowly deposited a crystalline powder melting with vigorous decomposition at 130—137°.

On boiling with water, the dry substance gradually dissolves, at the same time giving off a quantity of benzene vapour. From the following analyses and subsequent investigation, it would appear to be a mixture of ois- and trans-phenylbutanetricarboxylic acids containing half a mol. of benzene of crystallisation.

I. 0·1504 gave 0·3458 CO₂ and 0·0788 H₂O. $C = 62 \cdot 70$; $H = 5 \cdot 82$. II. 0·1454 ,, 0·3362 CO₂ ,, 0·0766 H₂O. $C = 63 \cdot 06$; $H = 5 \cdot 85$. $C_{10}H_{11}(COOH)_8 + \frac{1}{2}C_8H_6$ requires $C = 62 \cdot 95$; $H = 5 \cdot 57$ per cent.

 $\begin{array}{c} trans-Phenylbutan etricar boxylic~Acid,\\ COOH\cdot CH_2\cdot CH(COOH)\cdot CH(C_0H_5)\cdot CH_2\cdot COOH+\frac{1}{2}H_2O. \end{array}$

The solution of the benzene compound, after being thoroughly boiled until the last traces of benzene have been expelled, deposits a crystal-line solid on standing; this separates from water in well-defined prisms, melts with evolution of aqueous vapour at 195°, and consists of the trans-acid, the more soluble cis-modification remaining in solution.

I. 0·1920 gave 0·3993 CO₂ and 0·0898 H₂O. C=56·71; H=5·20. II. 0·1421 ,, 0·2991 CO₂ ,, 0·0713 H₂O. C=57·40; H=5·57. $C_{10}H_{11}(COOH)_8 + \frac{1}{2}H_2O$ requires C=56·72; H=5·41 per cent.

trans-Phenylbutanetricarboxylic acid is insoluble in benzene and light petroleum, but readily soluble in acetone and moist ether; owing to the ease with which it is converted into the corresponding anhydroacid, all attempts made to prepare the acid in an anhydrous state by heating it failed. The acid does not give an insoluble barium salt when a solution of its ammonium salt is mixed with barium chloride and boiled, and in this respect it differs from the corresponding cis-acid.

Anhydrophonylbutanetricarboxylic Acid, CH₂—CH·CH(C₆H₅)·CH₂·COOH. CO·O·CO

This anhydro-acid is readily prepared by boiling trans-phenylbutanetricarboxylic acid with acetyl chloride for 6 hours, and remains as a hard resin on evaporating the solution in a desiccator over potassium hydroxide. It may be obtained in a crystalline form by dissolving the resin in hot acetone and adding hot light petroleum until a

turbidity ensues; on cooling, the anhydro-acid separates in fine needles which melt at 134—135°.

0.2003 gave 0.4628 CO₂ and 0.0870 H₂O. C=63.01; H=4.80.
$$C_{13}H_{12}O_{5}$$
 requires C=62.90; H=4.83 per cent.

The anhydro-acid dissolves readily in boiling water, and the solution, on concentrating and cooling, deposits a crystalline mass of cis-phenyl-butanetricarboxylic acid which differs from the trans-acid in giving a characteristic barium salt, readily soluble in cold, but only sparingly so in hot water; a large quantity of this barium salt may be obtained from the filtrate of the trans-acid, which, as previously stated (p. 907), was prepared by boiling the benzene compound of the mixed acids with water, and, after all traces of benzene had been expelled, allowing the solution to remain for some time. The filtrate from the trans-acid, after being made strongly alkaline with ammonia, gives, on addition of barium chloride and boiling, a copious precipitate of the barium salt.

cis-Phenylbutanetricarboxylic Acid,
COOH·
$$CH_2$$
· $CH(COOH)$ · $CH(C_0H_0)$ · CH_2 · $COOH$.

This acid is prepared by dissolving the barium salt mentioned above in hydrochloric acid and extracting with ether. It crystallises from water in prisms closely resembling the *trans*-acid in appearance, but melts at 178—180°, and does not contain water of crystallisation.

I.
$$0.1544$$
 gave 0.3280 CO₂ and 0.0745 H₂O. C = 57.94 ; H = 5.36 . II. 0.1182 ,, 0.2518 CO₂ ,, 0.0518 H₂O. C = 58.14 ; H = 5.62 . C₁₀H₁₁(COOH)₈ requires C = 58.65 ; H = 5.26 per cent.

The cis-acid is more soluble in water than the trans-acid, but on boiling with acetyl chloride both give the same anhydro-acid melting at 134—135°.

The silver salt, $C_{10}H_{11}(COOAg)_8$, is obtained as a white, floculent precipitate on adding silver nitrate to a solution of the ammonium salt.

0.6584 gave 0.3521 Ag. Ag = 54.97.
$$C_{10}H_{11}(COOAg)_3$$
 requires Ag = 55.10 per cent.

On adding aniline to a solution of the anhydro-acid in benzene, a crystalline compound is formed which melts at 140°.

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LXXXIX.—Experiments on the Synthesis of Camphoric Acid. Part II.*

By H. A. Auden, W. H. Perkin, jun., and J. L. Rose.

In 1896, the view was first expressed by one of us (Perkin, Proceedings, 1896, 12, 191) that most of the decompositions of camphoric acid might readily be explained with the aid of the formula

and this formula for camphoric acid was afterwards independently suggested by Bouveault (Bull. Soc. Chim., 1897, [iii], 17, 990), and is now generally known on the continent as "Bouveault's formula." In view of the unusual difficulties which have been found to attend the determination of the constitution of camphoric acid by analytical methods, it was decided some years ago to undertake a long series of experiments with a view of preparing this acid synthetically. The present paper deals with the results which were obtained in an attempt to prepare an acid of the formula given above, and although this result so far has not been realised, our experiments have nevertheless led to the preparation and characterisation of a number of substances of considerable interest which are described in the following pages.

In attempting the synthesis, we proposed in the first place to prepare aa₁-methylisoamyl-a-hydroxysuccinic acid,

$$\begin{array}{c} \operatorname{CH_2} \\ \operatorname{CH_3}_2\operatorname{CH^{\bullet}} & \operatorname{CH_2} \\ \operatorname{CH-COOH,} \\ \operatorname{CH_3} \cdot \overset{\bullet}{\operatorname{C}}(\operatorname{OH}) \cdot \operatorname{COOH} \end{array}$$

as it was thought that it might be found possible to eliminate water at the points marked *, in which case the acid represented by the formula at the commencement of this paper would be obtained. It will be seen that this research is very much on the same lines as that carried out by Bentley and Perkin (Trans., 1898, 73, 45), who prepared isobutylmethylhydroxyglutaric acid,

$$\begin{array}{c|c} CH_2 & CH \cdot COOH \\ (CH_3)_2 CH^{\bullet} & \\ CH_3 \cdot C(OH)(COOH) \cdot CH_2 \end{array}$$

* Part I., Trans., 1898, 78, 45.

with a view of removing water at the points *, and of thus obtaining an acid of the formula

which may possibly be camphoric acid.

The latter change could, however, not be brought about, principally on account of the great tendency which the hydroxy-acid shows to pass into a lactone by the elimination of water between the COOH and OH groups situated in the γ -position, a possibility which is not present in the case of the hydroxy-acid which we are considering in this paper. After many unsuccessful attempts, we have ultimately succeeded in preparing methylisoamylhydroxysuccinic acid by the following series of reactions. Ethylic isoamylacetoacetate,

$$CH_8 \cdot CO \cdot CH(C_5H_{11}) \cdot COOC_2H_5$$

was first caused to combine with hydrogen cyanide by treating its solution in ether at a low temperature with potassium cyanide and hydrochloric acid, and in this way a good yield of *ethylic a-isoamyl-* $\beta\beta$ -hydroxycyanobutyrate, $CH_8 \cdot C(OH)(CN) \cdot CH(C_5H_{11}) \cdot COOC_2H_5$, was obtained.

When this substance is treated with alcohol and hydrochloric acid, the two most important products are methylisoamylhydroxysuccinimids,

$$CH_3 \cdot COH \cdot CO > NH$$

a solid, crystalline substance melting at 104°, and an oil which is doubtless ethylic methylisoamylhydroxysuccinate,

$$\begin{matrix} \mathbf{C_5H_{11} \cdot CH \cdot COOC_2H_5} \\ \mathbf{CH_8 \cdot C(OH) \cdot COOC_2H_5} \end{matrix}$$

The imide, on boiling with sodium carbonate, yields, in the first place, the corresponding amide, and this is then very slowly further decomposed with elimination of ammonia and formation of the methylisoamylhydroxysuccinic acid,

$$C_8H_{11} \cdot CH \cdot COOH$$

 $CH_8 \cdot C(OH) \cdot COOH$

which was required for our experiments. This interesting acid crystallises well, melts at 66°, and yields a silver salt of the formula $C_{10}H_{16}Ag_2O_5$, and its method of formation and the study of its properties leave no doubt that it has the constitution assigned to it here. When this acid is distilled, it readily loses water, and an oil passes over at about 260°, which, after careful investigation, has been found

to consist of methylisoamylmaleic anhydride, formed according to the equation

$$\begin{array}{ccc} \mathbf{C_b} \mathbf{H_{11}} \cdot \mathbf{CH} \cdot \mathbf{COOH} \\ \mathbf{CH_a} \cdot \mathbf{C(OH)} \cdot \mathbf{COOH} \end{array} = \begin{array}{cccc} \mathbf{C_b} \mathbf{H_{11}} \cdot \mathbf{C} \cdot \mathbf{CO} \\ \mathbf{CH_a} \cdot \mathbf{C} \cdot \mathbf{CO} \end{array} > 0 + 2\mathbf{H_2O},$$

that is to say, the anhydride of an unsaturated acid is formed, and not of the saturated acid containing a ring of five atoms which we had hoped to obtain.

Methylisoamylmaleic anhydride dissolves in potash solution, but on acidifying, the anhydride and not the acid separates, and, in this respect, the substance behaves exactly like xeronic acid,

$$C_2H_5 \cdot C \cdot COOH$$

 $C_2H_5 \cdot C \cdot COOH$

which, when set free from solutions of its salts, is obtained in the form of its anhydride.

When treated with aniline, methylisoamylmaleic anhydride yields an anil, $C_{16}H_{19}NO_2$ (m. p. 70°), and when boiled with hydriodic acid and phosphorus, it is readily reduced, with formation of a mixture of cis- and trans-methylisoamylsuccinic acids,

the former of which melts at 92° and the latter at 142° (compare W. Trevor Lawrence, Proc., 1899, 15, 163).

In continuation of our experiments, we next investigated the action of reducing agents on ethylic isoamylacetoacetate in order to determine whether the a-isoamyl- β -hydroxybutyric acid, CH₈·CH(OH)·CH(C₅H₁₁)·COOH, which is formed in this way would, on distillation, lose water with formation of a ring compound,

$$\begin{array}{cccc} \operatorname{CH}_2 & \operatorname{CH}_2 & \operatorname{CH}_2 \\ \operatorname{CH}_3 \cdot \operatorname{CH}(\operatorname{OH}) & \operatorname{CH} \cdot \operatorname{COOH} & = & \operatorname{CH}_3 \cdot \operatorname{CH} \cdot \operatorname{CH} \cdot \operatorname{COOH}, \end{array}$$

or whether, as in the case of methylisoamylhydroxysuccinic acid, an unsaturated acid, $\mathrm{CH_3}\text{-}\mathrm{CH:C(C_5H_{11})}\text{-}\mathrm{COOH}$, would be formed.

If the ring compound were formed, the synthesis would be most important, since, on the supposition that the formula for camphoric acid represented at the commencement of this paper is correct, the product would be dihydroisolauronolic acid (compare Trans., 1898, '73, 810).

On investigating the matter, it was found that the hydroxy-acid, on distillation, yields the unsaturated acid, and that apparently no trace of the ring acid is formed in this way.

The a-isoamylcrotonic acid, CH₈·CH:C(C₅H₁₁)·COOH, thus obtained

is a colourless oil which distils at 240°, and its constitution is proved by the fact that it yields isobutylacetic acid, C₄H₉·CH₂·COOH, on oxidation.

Lastly, we investigated the action of hydrogen cyanide on isoamylacetone, $C_5H_{11}\cdot CH_2\cdot CO\cdot CH_8$, and after hydrolysing the product we obtained in this way small quantities of a-hydroxy- β -iso-amylisobutyric acid, $C_5H_{11}\cdot CH_2\cdot C(OH)(CH_3)\cdot COOH$, which melts at 66° and is isomeric with the isoamylhydroxybutyric acid mentioned above. Unfortunately, the yield is scarcely more than 1 per cent. of the theoretical, and therefore we were unable to investigate it as completely as we could have wished.

Preparation and Hydrolysis of Ethylic a-Isoamyl- $\beta\beta$ -hydroxycyanobutyrate, $CH_0 \cdot C(CN)(OH) \cdot CH(C_0H_{11}) \cdot COOC_0H_0$.

In endeavouring to prepare this substance by the addition of hydrogen cyanide to ethylic isoamylacetoacetate, experiments were made under the most varied circumstances, in order to determine the best conditions, and ultimately it was found that the following method, which is very similar to that described by Haller and Held (Ann. Chim. Phys., 1891, [vi], 23, 145), gave the most satisfactory result. Ethylic isoamylacetoacetate (50 grams) is dissolved in ether (50 grams), finely powdered potassium cyanide (25 grams) added, and then the calculated quantity of hydrochloric acid (about 40 c.c. of the ordinary concentrated acid) gradually run in with constant shaking, the temperature being kept below -10° during the whole operation. After standing for 24 hours at the ordinary temperature, the ethereal solution is washed with water, dried over calcium chloride, and the ether distilled off, when a thick, yellow oil is obtained, which consists of crude ethylic isoamylhydroxycyanobutyrate, and in this form it was used in all subsequent experiments. The hydrolysis of this crude ethereal salt was carried out by two methods which give different results, namely, (a) by means of hydrochloric acid, and (b) by means of sulphuric acid.

(a) Hydrolysis by means of Hydrochloric Acid.—The crude cyanoethereal salt (100 grams) was dissolved in absolute alcohol (150 grams), and the whole saturated with hydrogen chloride, the temperature being kept below 20° by cooling with water. After standing overnight, the product was heated in a reflux apparatus on the water-bath for 2 hours, hydrogen chloride being passed through during the whole time, when large quantities of ammonium chloride separated. The alcoholic solution was poured into water and the oil, which separated, extracted with ether; the ethereal solution was washed with water and very dilute sodium carbonate solution and distilled in steam, in order to remove isoamylacetone, $C_6H_{11} \cdot CH_2 \cdot CO \cdot CH_2$. This substance, which

is always formed, and sometimes in considerable quantity, is evidently produced by the hydrolysis of the unchanged ethylic isoamylaceto-acetate present in the crude ethylic isoamylhydroxycyanobutyrate employed in these experiments. The oil remaining in the distillation flask may be treated in two ways: (a) it is shaken with dilute ammonia, and the aqueous solution, after filtering from the undissolved oil, is rapidly acidified, when a crystalline precipitate separates, which consists for the most part of methylisoamylhydroxysuccinimids (p. 914), or (b) the oil is boiled for about an hour with dilute sodium carbonate, when, after filtering and acidifying, a precipitate of methylisoamylhydroxysuccinamide is obtained (p. 914). In either case, the oil remaining undissolved, which still contains much nitrogen, is heated in a sealed tube with alcoholic hydrogen chloride for 5 hours at 150°.

After diluting with water and extracting with ether in the usual way, the oil which is obtained on distilling off the ether is fractionated under reduced pressure (20 mm.), and is thus easily separated into three fractions boiling at 60—90°, 120—130°, and 155—175° respectively. The first fraction, on distillation under ordinary conditions, yields a quantity of an oil boiling at 162—163°, and which was found to be isoamylacetons.

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0.1783 gave 0.4899 CO_2 and 0.2015 H_2O. C = 74.93; H = 12.56. C_5H_{11}\cdot CH_2\cdot CO\cdot CH_3 requires C = 75.0; H = 12.50 per cent.
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The second fraction was redistilled, when the greater portion passed over at 120° under 18 mm. pressure, and on analysis was found to consist of ethylic isoamylacetoacetate.

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0.2095 gave 0.5049 CO<sub>2</sub> and 0.1863 H_2O. C = 65.73; H = 9.88. CH_3 \cdot CO \cdot CH(C_5H_{11}) \cdot COOC_2H_5 requires C = 66.0; H = 10.0 per cent.
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On repeatedly fractionating the highest fraction, a large quantity of an oil was obtained which boiled remarkably constantly at 163° under 20 mm. pressure, and on analysis gave numbers agreeing fairly well with those required for the ethereal salt of an acid of the same composition as camphoric acid.

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0.2173 gave 0.5130 CO_2 and 0.1870 H_2O. C = 64.38; H = 9.56. 0.2029 , 0.4803 CO_2 , 0.1726 H_2O. C = 64.55; H = 9.45. C_8H_{14}(COOC_9H_5)_2 requires C = 65.62; H = 9.37 per cent.
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It will be shown later that this oil, although boiling so constantly, is a mixture of the ethereal salts of methylisoamylmaleic acid and methylisoamylhydroxysuccinic acid, the latter predominating.

(b) Hydrolysis by means of Sulphuric Acid.—After a considerable VOL. LXXV. 3 P

quantity of ethylic isoamylhydroxycyanobutyrate had been hydrolysed by means of hydrochloric acid, experiments were made with sulphuric acid in the hope that the hydrolysis could, in this way, be completed without the necessity of using sealed tubes, and this was found to be the case. The cyano-ethereal salt (100 grams) was dissolved in alcohol (200 grams), concentrated sulphuric acid (300 grams) was slowly added, and the mixture, after standing for 12 hours, heated for 8 hours on the water-bath; water was then added and the ethereal salt extracted with ether in the usual way. On fractionating the product under reduced pressure, isoamylacetone first passed over, but in less quantity than in the case of the hydrochloric acid hydrolysis; the greater portion of the residue then distilled between 155° and 175° under 20 mm. pressure, and, on examination, was found to have the same composition as the oil of this boiling point obtained in the case of the hydrochloric acid hydrolysis. A small quantity which distilled above 175° deposited, on standing, some crystals of methylisoamylhydroxysuccinimide. If, then, the object is to prepare this imide, the hydrochloric acid hydrolysis should be employed; but if, on the other hand, methylisoamylmaleic anhydride (p. 916) is required, then the sulphuric acid hydrolysis is much to be preferred as being less laborious.

 $aa_1\text{-Methylisoamyl-a-hydroxysuccinic acid,} \begin{array}{c} CH_3 \cdot C(OH) \cdot COOH \\ C_5H_{11} \cdot CH \cdot COOH \end{array}.$

It was stated in the previous section, that when ethylic isoamylhydroxycyanobutyrate is hydrolysed with alcohol and hydrochloric acid and the product extracted with ammonia, a solid substance separates on acidifying, which, on examination, has been found to be

methylisoamylhydroxysucoinimids, C₅H₁₁·CH—CONH. This substance crystallises from light petroleum in colourless needles, melts at 104°, and is readily soluble in alcohol, ether, and benzene, but only sparingly so in cold, light petroleum and water. When heated in small quantities, it distils, apparently without decomposition.

0.1631 gave 0.3610 CO₂ and 0.1280 H₂O. C=60.36; H=8.72. 0.2482 ,, 14.65 c.c. nitrogen at 20° and 766 mm. N=6.88. $C_{10}H_{17}NO_8$ requires C=60.30; H=8.54; N=7.04 per cent.

When methylisoamylhydroxysuccinimide is boiled with sodium carbonate solution, it gradually dissolves and, on acidifying, the corresponding methylisoamylhydroxysuccinamide is obtained as a white, sparingly soluble precipitate which crystallises from water in plates and melts at 183°,

0.1682 gave 0.3395 CO₂ and 0.1377 H₂O. C = 55.04; H = 9.09. 0.1606 , 9.4 c.c. nitrogen at 17° and 748 mm. N = 6.72. $C_{10}H_{10}NO_4$ requires C = 55.29; H = 8.75; N = 6.45 per cent.

The amide is readily soluble in alcohol, sparingly so in cold water, ether, or benzene, and almost insoluble in light petroleum. When heated in a test tube, it gives off water and an oil distils which only partially solidified.

Methylisoamylhydroxysuccinamide is readily decomposed by boiling with potash solution and ammonia is evolved, but even when the potash is only in slight excess, some secondary decomposition takes place, and the resulting acid is difficult to obtain in a crystalline form. If, however, the amide is boiled with strong sodium carbonate solution, ammonia is only very slowly evolved, and even after 24 hours much of the compound remains unchanged and is precipitated on acidifying the alkaline liquid. The filtrate made alkaline with ammonia gives, on boiling with calcium chloride, a white, crystalline precipitate of calcium methylisoamylhydroxysuccinate, which is collected by the aid of a vacuum pump and washed with hot water, this salt being less soluble in hot than in cold water.

In order to obtain the free acid, the calcium salt was dissolved in dilute hydrochloric acid and the solution extracted several times with pure ether; the ethereal solution, after drying over calcium chloride and evaporating, yielded a thick oil which, on standing over sulphuric acid in a vacuum desiccator, completely solidified. For the analysis, this acid was further purified by recrystallisation from a mixture of benzene and light petroleum.

I. 0·1896 gave 0·3863 CO_2 and 0·1430 H_2O . C=55·56; H=8·38. II. 0·1701 , 0·3441 CO_2 , 0·1269 H_2O . C=55·17; H=8·29. $C_{10}H_{18}O_5$ requires C=55·04; H=8·26 per cent.

Methylisoamylhydroxysuccinic acid melts at 66° and is very readily soluble in water, forming a strongly acid solution. It also dissolves readily in alcohol, and moderately so in benzene, but is almost insoluble in light petroleum.

The silver salt, $C_{10}H_{16}Ag_2O_5$, is obtained as a white precipitate on adding silver nitrate to a neutral solution of the ammonium salt.

0.2076 gave 0.2141 CO₂ and 0.0708 H_2O . C = 28.12; H = 3.78. 0.2380 , 0.1181 Ag. Ag = 49.64. $C_{10}H_{16}Ag_2O_5$ requires C = 27.91; H = 3.72; Ag = 50.0 per cent.

A neutral solution of the ammonium salt of the acid shows the following behaviour with reagents. *Barium chlorids* gives a white, amorphous precipitate which becomes crystalline on boiling, and is

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very sparingly soluble, even in boiling water. Calcium chloride forms no precipitate in the cold, but, on boiling, a very sparingly soluble, crystalline calcium salt separates. Copper sulphate gives a pale blue, amorphous precipitate, and lead acetate, a white, amorphous precipitate.

Methylisoamylmaleic Anhydride,
$$C_5H_{11}$$
· C · CO > O .

It was stated on p. 913 that the principal product of the hydrolysis of ethylic isoamylhydroxycyanobutyrate with alcoholic hydrochloric or sulphuric acid was an oil boiling constantly at 163° under 20 mm. pressure, which, on analysis, gave numbers agreeing approximately with those required by the formula $C_{\rm e}H_{\rm 1d}({\rm COOC_0H_s})_{\rm e}$.

This oil was hydrolysed by boiling with alcoholic potash for 2 hours, when, on adding water, a small quantity of oil separated, which, on examination, was found to consist of isoamylacetone. This oil was removed by extraction with ether, the alkaline solution was then acidified and repeatedly extracted with pure ether when, after drying over calcium chloride and evaporating, a thick, yellow oil was obtained which, even after long standing over sulphuric acid in a vacuum desiccator, showed no signs of crystallising. Ultimately, it was found that this product contained a small quantity of an acid which formed a sparingly soluble barium salt, and therefore the whole quantity was dissolved in a slight excess of ammonia and boiled with barium chloride. The insoluble barium salt was collected, washed with water, and dissolved in dilute hydrochloric acid, when, on extracting with ether, an acid was obtained which, on standing, solidified. The solid mass was spread on porous porcelain to remove traces of oily mother liquor, and recrystallised from a mixture of benzene and light petroleum. In this way glistening needles were obtained which melted at 66° and evidently consisted of methylisoamylhydroxysuccinic acid, as the following analysis and a careful comparison with a specimen of this acid, prepared as explained on p. 915, conclusively showed:

0.1346 gave 0.2708
$$CO_2$$
 and 0.1 H_2O . $C = 54.87$; $H = 8.25$. $C_{10}H_{18}O_5$ requires $C = 55.04$; $H = 8.26$ per cent.

The filtrate from the sparingly soluble barium salt was acidified, extracted with ether, and, after drying over calcium chloride and distilling off the ether, the residual oil fractionated under reduced pressure. After several distillations, an oil was obtained which boiled constantly at 142° under 16 mm. pressure, and which, on careful investigation, was found to consist of methylisoamylmaleic anhydride.

0.1856 gave 0.4460 CO₂ and 0.1348 H₂O. C = 65.54; H = 8.07. $C_{10}H_{14}O_3$ requires C = 65.93; H = 7.69 per cent.

This anhydride is insoluble in cold sodium carbonate solution, but on warming with caustic soda it rapidly dissolves, and on acidifying and extracting with ether, an oil is obtained which is not the free acid, but the anhydride, since it is insoluble in sodium carbonate and, after standing for some time over sulphuric acid in a vacuum desiccator, it yielded the following results on analysis:

0.1860 gave 0.4436 CO_2 and 0.1333 H_2O . C=65.04; H=7.96. Methylisoamylmaleic anhydride requires C=65.93; H=7.69 per cent.

In order to obtain further evidence as to the mode of formation of methylisoamylmaleic anhydride, experiments were made with the object of determining whether this substance is formed when methylisoamylhydroxysuccinic acid is distilled at the ordinary pressure. On cautiously heating about 5 grams of the pure hydroxy-acid in a small fractionating flask, water was first given off and then the temperature rapidly rose to 255°, nearly the whole distilling between this temperature and 265°; on refractionating, an oil was obtained boiling constantly at 260—262°, which was insoluble in sodium carbonate solution.

That this oil was methylisoamylmaleic anhydride was shown by converting it into the anil which melted at 70°, and was identical in properties with the anil of methylisoamylmaleic acid described below. An equation representing the formation of the anhydride from methylisoamylhydroxysuccinic acid is given in the introduction.

Anil of Methylisoamylmaleic Acid,
$$C_{6}H_{11}$$
. C·CO NC₆H₅.

When a solution of methylisoamylmaleic anhydride in benzene is mixed with aniline, there is very little rise of temperature and no anilic acid separates on standing; if, however, the benzene is removed by evaporation on the water-bath and the residue then stirred with dilute hydrochloric acid, it gradually solidifies. The crystalline mass is spread on porous porcelain until quite free from oily mother-liquor, and then purified by crystallisation from dilute alcohol, from which it separates in glistening plates which melt at 70°.

This anil is readily soluble in ether, benzene, warm alcohol, or light petroleum (b. p. 80—90°), sparingly so in water, and insoluble in sodium carbonate solution. When heated in small quantities, it distils apparently without decomposition.

Reduction of Methylisoamylmaleic Anhydride. Formation of cis- and CH₈·CH·COOH trans-Methylisoamylsuccinic Acids, C₅H₁₁·CH·COOH

When methylisoamylmaleic anhydride (4 grams) is heated in a reflux apparatus on the sand-bath with fuming hydriodic acid (20 grams) and amorphous phosphorus (2 grams), reduction readily takes place, and after boiling for 8 hours and allowing to cool, a quantity of a crystalline substance separates. The product is diluted with twice its bulk of water, repeatedly extracted with ether, and the ethereal solution, after washing with dilute sodium bisulphite to remove iodine, dried over calcium chloride and evaporated, when a solid residue is obtained which consists of a mixture of the cis- and trans-acids. When this is stirred with light petroleum (b. p. 70—90°), the cis-acid dissolves, and leaves the almost pure trans-acid which, after recrystallising from water, is obtained in colourless prisms melting at 142°.

0.1686 gave 0.3676 CO₂ and 0.1337 H₂O. C = 59.46; H = 8.81. $C_{10}H_{18}O_4$ requires C = 59.40; H = 8.91 per cent.

The light petroleum mother liquors of this acid, on evaporation, give a solid residue which crystallises from hydrochloric acid in plates melting at 92°, and consists of the cis-modification.

0.1534 gave 0.3328 CO_2 and 0.124 H_2O . C=59.16; H=8.98. $C_{10}H_{18}O_4$ requires C=59.40; H=8.91 per cent.

These acids agree in all their properties with the cis- and transmodifications of methylisoamylsuccinic acid which W. Trevor Lawrence has obtained by another process (Proc., 1899, 15, 163).

Reduction of Ethylic Isoamylacetoacetate. Formation of a-Isoamyl- β -hydroxybutyric Acid, $CH_3 \cdot CH(OH) \cdot CH(C_5H_{11}) \cdot COOH$.

In investigating this reduction, ethylic isoamylacetoacetate (50 grams) was dissolved in alcohol (250 c.c.) and water (100 c.c.), and then treated in flat dishes with 3 per cent. sodium amalgam (2 kilos.) at ordinary temperatures, small quantities of water being added from time to time to facilitate the decomposition of the amalgam. After standing for 2 days and pouring into water, very little oil separated, showing that hydrolysis, as well as reduction, had taken place, and, in order to isolate the hydroxy-acid, the product was evaporated on the water-bath until free from alcohol, acidified, and extracted several times with pure ether. The ethereal solution was dried over calcium chloride and evaporated, when a thick oil was obtained, which, even on long standing, showed no signs of crystallising, but which can be

readily purified by conversion into the characteristic crystalline copper salt. In order to prepare this, the acid is dissolved in a slight excess of ammonia, and the moderately* dilute solution mixed with excess of copper sulphate and allowed to stand, when a beautifully crystalline, dark blue copper salt separates, which is collected, decomposed by hydrochloric acid, and the acid again extracted with ether. The oily acid thus obtained, after standing for some days over sulphuric acid in a vacuum desiccator, gave the following numbers on analysis:

0.1820 gave 0.4125 CO₂ and 0.1655 H_2O . C = 61.81; H = 10.10. $CH_3 \cdot CH(OH) \cdot CH(C_5H_{11}) \cdot COOH$ requires C = 62.07; H = 10.34 per cent.

Isoamylhydroxybutyric acid is a thick, colourless oil, sparingly soluble in water, which, as shown below, distils under reduced pressure unchanged, but at the ordinary pressure decomposes on distillation into isoamylcrotonic acid and water.

The silver salt, C₉H₁₇AgO₃, was prepared by adding silver nitrate to a neutral solution of the ammonium salt. It is a white, amorphous precipitate, which, on analysis, gave the following result:

0.1233 gave 0.0477 Ag. Ag = 38.68. $C_9H_{17}AgO_8 \ \ {\rm requires} \ \ Ag = 38.43 \ \ {\rm per \ cent}.$

A neutral and moderately strong solution of the ammonium salt gives a white, gelatinous precipitate with barium chloride, but no precipitate with calcium chloride.

a-Isoamylerotonic Acid, CHg. CH:C(C5H11)·COOH.

When isoamylhydroxybutyric acid is distilled under reduced pressure (50 mm.), it passes over at about 195° without decomposition, as the following analysis of the distillate shows:

0.1755 gave 0.4 CO₂ and 0.1587 H₂O. C = 62.16; H = 10.04. CH₈·CH(OH)·CH(C₅H₁₁)·COOH requires C = 62.07; H = 10.34 per cent.

If, however, the distillation is conducted under the ordinary pressure, water is eliminated, and an oil passes over at 235—250°; this consists of crude isoamylcrotonic acid, and by repeatedly refractionating an oil is obtained boiling fairly constantly at about 240°. The analysis gave rather low results, due to some slight impurity, which could not be removed by fractionation.

0.1832 gave 0.4577 CO₂ and 0.1593 H₂O. C=68.13; H=9.66. 0.1336 ,, 0.3337 CO₂ ,, 0.1182 H₂O. C=68.12; H=9.83. CH₈·CH:C(C₅H₁₁)·COOH requires C=69.23; H=10.25 per cent.

^{*} It is important that the solution should not be too concentrated, otherwise the copper salt is apt to separate in resinous clumps.

Isoamylcrotonic acid is sparingly soluble in water, but dissolves readily in sodium carbonate, and the solution decolorises permanganate at once at the ordinary temperature.

The silver salt, obtained in the usual way, is a white, sparingly soluble, amorphous precipitate.

0.1956 gave 0.0815 Ag. Ag = 41.66. $C_9H_{15}AgO_2$ requires Ag = 41.06 per cent.

Oxidation of Isoamylciotonic Acid. Formation of Isobutylacetic Acid.—In investigating this oxidation, about 20 grams of the acid, in quantities of 5 grams at a time, were dissolved in a slight excess of very dilute sodium carbonate, and treated with potassium permanganate at 0° until the pink colour remained permanent for some hours; the excess of permanganate was then destroyed by sodium sulphite, and the filtrate from the manganese precipitate evaporated to a small bulk. On acidifying, an oily acid was precipitated, which was extracted with ether; the ethereal solution was very carefully dried over calcium chloride, evaporated, and the residual oil several times fractionated. In this way an acid was obtained boiling constantly at 202°, and showing all the properties of isobutylacetic acid, which, according to Lieben and Rossi (Annalen, 1871, 159, 76), boils at 199.7° under 732 mm. pressure. The silver salt of this acid, prepared in the usual way, gave the following results on analysis:

0.2129 gave 0.2510 CO₂ and 0.0936 H₂O. C = 32.15; H = 4.88. 0.2021 , 0.0974 Ag. Ag = 48.19. $C_6H_{11}AgO_2$ requires C = 32.28; H = 4.93; Ag = 48.43 per cent.

This acid, which is isomeric with the a-isoamyl- β -hydroxybutyric acid described on p. 919, was obtained in small quantities in the following way:

Isoamylacetone (40 grams) was dissolved in dry ether (40 grams), finely-powdered potassium cyanide (30 grams) added, and then the calculated quantity of hydrochloric acid run in drop by drop, the whole being kept at -10° during the operation. After standing for 24 hours, the ethereal solution was washed and evaporated, and the residual oil hydrolysed by means of alcoholic hydrochloric acid, the method employed being exactly the same as that described on p. 912. On fractionating the product under reduced pressure (20 mm.), much unchanged isoamylacetone first passed over, then the temperature rose rapidly to 150°, most of the oil passing over between this and 170°, and on refractionating this, an oil was obtained boiling almost

constantly at 156° under 20 mm. pressure. Analysis showed that the composition of this oil varies, two different preparations giving respectively $C=79\cdot27$, $H=12\cdot41$, and $C=76\cdot27$, $H=11\cdot97$, whereas if the oil had consisted entirely of ethylic isoamylhydroxyisobutyrate, $C_5H_{11}\cdot CH_2\cdot C(OH)(CH_8)\cdot COOC_2H_5$, as was expected, the percentages would have been $C=65\cdot34$, $H=10\cdot89$.

The substance therefore contains some compound very rich in carbon and hydrogen, possibly produced by the condensation of two mols. of isoamylacetone under the influence of the reagents employed. On hydrolysing the oil with alcoholic potash, a large quantity of isoamylacetone was produced; this was removed by extracting with ether, the alkaline solution was then evaporated until free from alcohol, acidified, and repeatedly extracted with ether. After drying over calcium chloride and distilling off the ether, a small quantity of an oily acid was obtained, which soon solidified, and crystallised from light petroleum in glistening plates melting at 76°.

0.1318 gave 0.3 CO₂ and 0.1253 H_2O . C = 62.07; H = 10.56. $C_9H_{18}O_3$ requires C = 62.07; H = 10.34 per cent.

The silver salt, C₉H₁₇AgO₃, was prepared from the neutral solution of the ammonium salt by adding silver nitrate. It is a white, amorphous precipitate, which, on analysis, gave the following result:

0.0937 gave 0.0364 Ag. Ag = 38.84. $C_9H_{17}AgO_8$ requires Ag = 38.43 per cent.

There can be no doubt that this interesting acid is β -isoamyla-hydroxyisobutyric acid, but as the yield obtained by the method described above is only 1 per cent. of the isoamylacetone employed, it could not be investigated in more detail.

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XC.—The Action of Ethylene Dibromide and Trimethylene Dibromide on the Sodium Compound of Ethylic Cyanacetate.

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In investigating the derivatives of tri- and tetra-methylene, one of the greatest difficulties met with was the smallness of the yield obtained in the reactions employed in their preparation; thus the amount of ethylic trimethylenedicarboxylate produced by the action of ethylene dibromide on the sodium compound of ethylic malonate

is seldom more than 10 per cent. of the theoretical. During the course of some researches on the action of the ethereal salts of unsaturated acids on ethylic malonate, it was found that the yield of condensation product was very largely increased when ethylic cyanacetate was substituted for ethylic malonate (compare Perkin and Thorpe, Trans., 1899, 75, 50), and this led us to institute experiments with the object of determining whether a similar increase in the yield might not be obtained by allowing ethylene dibromide and trimethylene dibromide to react with the sodium compound of ethylic cyanacetate in place of ethylic sodiomalonate; this has been found to be the case.

When the sodium compound of ethylic cyanacetate, suspended in alcohol, is digested with ethylene dibromide, the reaction proceeds normally with formation of ethylic cyanotrimethylenecarboxylate,

$$\begin{split} 2 \text{NaCH}(\text{CN}) \cdot \text{COOC}_2 \text{H}_5 + \text{BrCH}_2 \cdot \text{CH}_2 \text{Br} = \\ \text{CH}_2 > \text{C}(\text{CN}) \cdot \text{COOC}_2 \text{H}_5 + \text{CH}_2(\text{CN}) \cdot \text{COOC}_2 \text{H}_5 + 2 \text{NaBr}, \end{split}$$

and the yield of this substance is over 50 per cent. of the theoretical.

This ethereal salt, which is a colourless oil boiling at 210—211°, is easily hydrolysed by alcoholic potash, yielding in the first place a crystalline acid, C₅H₅NO₂, which melts at 149°, gives a silver salt of the formula C₅H₄AgNO₂, and thus is apparently cyanotrimethylene-CH₂

carboxylic acid, CH₂>C(CN)·COOH.

When this acid is heated, it sublimes to some extent unchanged, but the bulk of it decomposes with much charring and without the formation of cyanotrimethylene, $\stackrel{CH_2}{CH_2}$ CH·CN. Since, under similar conditions, the corresponding cyanotetramethylenecarboxylic acid, $\stackrel{CH_2}{CH_2}$ ·C(CN)·COOH (p. 932), is almost quantitatively converted into carbon dioxide and cyanotetramethylene, it seemed doubtful whether the two acids could be analogously constituted, and we were therefore for some time of the opinion that the substance described as cyanotrimethylenecarboxylic acid might in reality be the isomeric imide of trimethylenedicarboxylic acid, $\stackrel{CH_2}{CH_2}$ CONH, a substance which would also give a silver salt of the formula $C_5H_4NO_2Ag$. The solution of the substance in water, however, is strongly acid to

litmus, and readily decomposes carbonates, properties which would hardly be shown by an imide; we have therefore assumed in this paper that it is cyanotrimethylenecarboxylic acid, and additional experiments will be made with the object of obtaining further information

in explanation of the remarkable difference in properties exhibited by this acid and cyanotetramethylenecarboxylic acid.

When cyanotrimethylenecarboxylic acid is hydrolysed by boiling with excess of aqueous potash, it is converted into trimethylenedicarboxylic

acid, CH_2 $C(COOH)_2$, consequently this acid, which formerly could be obtained only in small quantity by starting with ethylic malonate, is now a substance comparatively easy of preparation.

When ethylene dibromide reacts with the sodium compound of ethylic malonate, there is always produced, besides ethylic trimethylenedicarboxylate, a small quantity of ethylic butanetetracarboxylate,

$$\begin{aligned} 2 \mathrm{CHNa}(\mathrm{COOC_2H_5})_2 + \mathrm{BrCH_2} \cdot \mathrm{CH_2Br} = \\ & (\mathrm{COOC_2H_5})_2 \mathrm{CH} \cdot \mathrm{CH_2} \cdot \mathrm{CH}(\mathrm{COOC_2H_5})_2 + 2 \mathrm{NaBr}, \end{aligned}$$

the latter being easily separated from the former by distillation in steam. When ethylic cyanacetate is substituted for ethylic malonate in this reaction, a similar behaviour was noticed, as on distilling the product in steam, a quantity of oil was left in the distillation flask, and on cooling solidified. This substance which crystallises from alcohol in glistening prisms (m. p. 119.5°), gives, on analysis, numbers agreeing with those required for the formula $C_0H_{12}N_2O_4$, and since, on hydrolysis, it is almost quantitatively converted into adipic acid, its constitution is evidently represented by the formula $CN \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CN) \cdot COOC_2H_5$, which is that of ethylic addicyanovalerate. The formation of this substance is somewhat remarkable, and may be assumed to take place in two stages. In the first place, ethylic dicyanobutanedicarboxylate is produced,

$$\begin{aligned} \text{COOC}_2\mathbf{H}_5 \cdot \text{CH}(\text{CN}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{COOC}_2\mathbf{H}_5 + \mathbf{H}_2\text{O} &=\\ \text{CO}_2 + \text{C}_2\mathbf{H}_5 \cdot \text{OH} + \text{CN} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{COOC}_2\mathbf{H}_5. \end{aligned}$$

This substance should form a sodium compound which, by treatment with alkyl iodides, &c., and subsequent hydrolysis and elimination of carbonic anhydride, should yield mono-substituted adipic acids, a synthesis which would be of much value, since these acids are, at the present time, exceedingly difficult to prepare.

When the sodium compound of ethylic cyanacetate is mixed with alcohol and trimethylene dibromide, a vigorous reaction takes place, and ethylic cyanotetramethylenecarboxylate is formed thus:

$$\begin{split} \mathbf{2NaCH}(\mathbf{CN}) \cdot \mathbf{COOC}_2\mathbf{H}_5 + \mathbf{BrCH}_2 \cdot \mathbf{CH}_2 \cdot \mathbf{CH}_2 \mathbf{Br} = \\ \mathbf{CH}_2 \cdot \mathbf{CH}_3 \\ \mathbf{CH}_2 \cdot \mathbf{C(CN)} \cdot \mathbf{COOC}_2\mathbf{H}_5 + \mathbf{CH}_2(\mathbf{CN}) \cdot \mathbf{COOC}_2\mathbf{H}_5 + \mathbf{2NaBr}. \end{split}$$

The ethereal salt, of which a very good yield is obtained in this way, is, on hydrolysis, first converted into the corresponding cyanotetramethylenecarboxylic acid, ${\rm CH_2 \cdot C(CN) \cdot COOH}$ (m. p. 69°), and this, on boiling with aqueous potash, yields tetramethylenedicarboxylic acid, ${\rm CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2$

When cyanotetramethylenecarboxylic acid is carefully heated, it sublimes unchanged; but if slowly distilled, it decomposes completely with evolution of carbon dioxide and formation of cyanotetramethylene, CH₂·CH₂. This interesting substance is a colourless oil boiling at 148—149°, which, on hydrolysis, is quantitatively converted into tetramethylenecarboxylic acid, CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·CH₂·COOH

In the reaction between the sodium compound of ethylic cyanacetate and trimethylene dibromide, an oily substance is formed which is not volatile in steam, and decomposes on distillation. Since this oil, on hydrolysis, yields pimelic acid, it is evidently either ethylic dicyanopentanedicarboxylate,

 ${\rm COOC_2H_5 \cdot CH(CN) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CN) \cdot COOC_2H_5,}$ or ethylic ac-dicyanocaproate,

CN·CH₂·CH₂·CH₂·CH₂·CH(CN)·COOC₂H₅, and experiments are in progress with the object of determining its constitution.

EXPERIMENTAL.

Action of Ethylene Dibromide on Ethylic Sodiocyanacetate. Formation of Ethylic Cyanotrinethylenecarboxylate, $CH_2 > C(CN) \cdot COOEt$, and of Ethylic $CH_2 \cdot CH_2 \cdot$

Ethylic Cyanotrimethylenecarboxylate.—The following method has been found to give the best results in the preparation of this compound: 5 grams of sodium are dissolved in 70 grams of absolute alcohol, and when the liquid is quite cold, 25 grams of ethylic cyanacetate are added. After the ethylic sodiocyanacetate has separated, 25 grams of ethylene dibromide are poured in and the mixture carefully heated to boiling on the water-bath in a reflux apparatus. A vigorous reaction sets in, which is sufficient to keep the liquid

boiling for 2-3 minutes. The decomposition is then complete, and a few drops of the liquid, diluted with water, give a neutral reaction with litmus paper.

In order to isolate the product, the alcohol is distilled off and the residue treated with sufficient water to dissolve the sodium bromide. After extracting with ether, washing the ethereal solution with water and dilute potassium carbonate solution (which removes all the red colouring matter), drying over calcium chloride, and distilling off the ether, an almost colourless oil remains, which is next fractionally distilled in steam. The first part of the distillate contains any unchanged ethylene dibromide, and as soon as this ceases to come over, the receiver is changed and the distillation continued so long as oily drops continue to be carried over. This portion of the distillate contains a mixture of ethylic cyanacetate and cyanotrimethylenecarboxylate. A small quantity of a thick oil, which remains in the distillation flask, solidifies on cooling and consists of crude ethylic ad-dicyanovalerate. The steam distillate is now saturated with ammonium sulphate and extracted with ether, the ethereal solution dried over calcium chloride, the ether distilled off, and the residual oil fractionated 2 or 3 times under ordinary pressure. In this way, ethylic cyanotrimethylenecarboxylate is ultimately obtained as a colourless liquid boiling at 210-211° under 766 mm. pressure.

0.1271 gave 0.2784 CO₂ and 0.0774 H₂O. C = 59.73; H = 6.77. 0.2614 , 22.6 c.c. of nitrogen at 18.5° and 770 mm. N = 10.09. $C_7H_0NO_9$ requires C = 60.41; H = 6.47; N = 10.09 per cent.

Cyanotrimethylenecarboxylic Acid,
$$CH_2 \sim C(CN) \cdot COOH$$
.

In order to prepare this acid, 3 grams of ethylic cyanotrimethylenecarboxylate, dissolved in 10 c.c. of methylic alcohol, were mixed with a slight excess of cold methyl alcoholic potash containing a little water, when hydrolysis took place very rapidly. The excess of caustic alkali was neutralised with carbon dioxide, and the alcohol then completely removed by evaporation on the water-bath; the residue was dissolved in water, acidified with dilute sulphuric acid, saturated with ammonium sulphate, and extracted 10 times with pure ether. After drying the ethereal solution over anhydrous sodium sulphate, the bulk of the ether was distilled off. and the concentrated solution left to crystallise over sulphuric acid: by this means, the acid was obtained in long, colourless prisms which were nearly pure and melted at 145-147.5°. The crystals were pressed on a porous plate to free them from adherent oily matter,

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crystallised from a mixture of ether and light petroleum (b. p. 60—80°), and dried at 100°.

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0.2576 gave 0.5142 CO<sub>2</sub> and 0.1119 H<sub>2</sub>O. C = 54.43; H = 4.82. 0.1867 ,, 21.3 c.c. of nitrogen at 19.5° and 738 mm. N = 12.69. C_5H_5NO_2 requires C = 54.31; H = 4.53; N = 12.64 per cent.
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Cyanotrimethylenecarboxylic acid melts at 149°, and, if carefully heated, most of it may be sublimed unchanged. Above 173°, however, it begins to decompose with evolution of carbon dioxide, but no volatile distillate is obtained as in the case of the corresponding cyanotetramethylenecarboxylic acid (p. 932). It is very soluble in water, and the solution reacts strongly acid to litmus paper. Warm ether and benzene dissolve it rapidly, but it is sparingly soluble in light petroleum. The yield of cyanotrimethylenecarboxylic acid, calculated from the ethylic cyanacetate employed in the synthesis, is as much as 50 per cent. of the theoretical. With ferric chloride, a neutral solution of the ammonium salt gives a brown precipitate, which dissolves on gently warming to a clear, red liquid; on boiling, a brown, fluffy precipitate is obtained, which after this cannot be redissolved.

The silver salt, C₅H₄NO₂Ag, was prepared by dissolving the acid in water and shaking with an excess of freshly-prepared silver carbonate; the whole was then warmed carefully to 50°, and, after cooling, filtered. The liquid cannot be concentrated on the water-bath, as, under these circumstances, the salt undergoes decomposition. The solution was therefore allowed to evaporate in a vacuum at the ordinary temperature, when the silver salt separated in the course of several days in lustrous prisms.

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0.1189 gave 0.0588 Ag. Ag = 49.45
0.0884 ,, 0.0438 Ag. Ag = 49.43
C_5H_4NO_9Ag requires Ag = 49.52 per cent.
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The barium salt was prepared by dissolving barium carbonate in an aqueous solution of the acid. It is left as a colourless syrup on evaporating nearly to dryness, but on cooling, this solidifies to a hard cake of prisms which was powdered and dried at 150—160° for analysis.

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0.2131 gave 0.1356 BaSO<sub>4</sub>. Ba = 37.40.
0.2050 ,, 0.1307 BaSO<sub>4</sub>. Ba = 37.50.
(C_5H_4NO_2)_2Ba + \frac{1}{2}H_2O requires Ba = 37.43 per cent.
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Amide of Cyanotrimethylenecarboxylic Acid, CH₂C(CN)·CO·NH₂.

—In order to prepare this substance, 2 grams of ethylic cyanotrimethylenecarboxylate were shaken with concentrated aqueous

ammonia (sp. gr. 0.88). After $1\frac{1}{2}$ hours the separation of the amide in white, glistening needles had begun, and was complete in about 7 hours. The crystals, which melted at 160° , were collected, dried at 120° , and analysed.

0.1838 gave 41.5 c.c. of nitrogen at 17.5° and 736 mm. N = 25.30. $C_5H_6N_2O$ requires N = 25.50 per cent.

Attempts to Prepare Cyanotrimethylene.

The following experiments were made with the object of preparing cyanotrimethylene, but were unsuccessful.

- (i) 2 grams of cyanotrimethylenecarboxylic acid were distilled from a small retort in a current of carbon dioxide. The substance melted and partly sublimed, and as the temperature was gradually raised above 173°, decomposition set in with much charring, and became very rapid as the temperature approached 200°, but very little or no volatile oil was produced.
- (ii) 0.5 gram was heated in a closed tube at 180° with 1 c.c. of water for an hour. On opening the tube, pressure of gas was noticed, and, on examination, this was found to be due in part to carbon dioxide. The brownish-coloured liquid was distilled in steam, but the distillate contained only ammonia. The residue was evaporated on the water-bath and left a brown oil soluble in water with an acid reaction.
- (iii) A small quantity of the powdered silver salt was carefully heated; very little charring occurred, and an oil was given off which condensed to a crystalline mass on the cooler parts of the tube.

Conversion of Cyanotrimethylenecarboxylic Acid into Trimethylenedicarboxylic Acid.

The pure cyano-acid was dissolved in concentrated aqueous potash and the solution boiled in a reflux apparatus, when rapid evolution of ammonia was at once noticed, and at the end of 6 hours the liquid was allowed to cool, acidified with dilute sulphuric acid, saturated with ammonium sulphate, and extracted 12 times with pure ether. The ethereal solution was dried over anhydrous sodium sulphate, the bulk of the ether distilled off, and the concentrated solution set aside to crystallise. By this means, trimethylenedicarboxylic acid was obtained in quantity melting at 133—136°, and with this the following characteristic derivatives were prepared.

(i) 3 grams were dissolved in a little concentrated aqueous hydrobromic acid of sp. gr. 1.83, when, on cooling, the whole set to a white, solid cake. This was spread on a porous plate to drain, and purified

by crystallisation from chloroform. In this way, the characteristic crystals of bromethylmalonic acid, melting at 116°, were obtained.

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0.2517 gave 0.2250 AgBr. Ag = 38.02.
0.1884 ,, 0.1694 AgBr. Ag = 38.27.
BrCH<sub>2</sub>·CH<sub>2</sub>·CH(COOH)<sub>2</sub> requires Br = 37.91 per cent.
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(ii) 0.7 gram was converted into the acid barium salt, which is recommended by Fittig and Röder for the identification of the acid. The salt crystallised from aqueous solutions in prisms, and had all the properties ascribed to it by these observers.

Ethylic ab-Dicyanovalerate, CN·CHoCHoCHoCHoCH(CN)·COOCoHo. The following method of preparation has been found to give the best yield of this compound: 59 grams of ethyl sodiocyanacetate, suspended in 140 grams of alcohol, are heated with 41 grams of ethylene dibromide for 5 hours in a soda-water bottle at 100°. When cool, the contents are transferred to a flask, the alcohol distilled off, and the residue treated with sufficient water to dissolve the sodium bromide. The liquid is extracted with ether, and the ethereal solution washed several times with water and dilute potassium carbonate solution, by which means the deep red colour of the solution may be entirely removed. After drying over calcium chloride and distilling off the ether, a yellowish-green liquid is left, which, on standing in a cool place, gradually deposits the bulk of the ethylic ad-dicyanovalerate in a crystalline form. The quickest method of isolating the substance consists, however, in distilling the crude product in steam, when ethylic cyanacetate and cyanotrimethylenecarboxylate distil over, leaving an oily residue which solidifies to a mass of prisms. water is poured off and the crystals, after being freed from oily impurities by washing with a small quantity of alcohol, are crystallised from a mixture of alcohol and light petroleum (b. p. 60-80°). this way, the substance may be obtained almost colourless, although the crystals usually have a yellowish tinge. The crystals, obtained by setting aside the original, yellowish-green liquid to cool, invariably have a greenish tinge which no amount of recrystallisation will remove. In the form of powder, however, both varieties are white. The sample for analysis was dried at 100°; it then melted at 119.5°, and gave on analysis the following numbers:

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0.2364 gave 0.5180 CO_2 and 0.1446 H_2O. C=59.76; H=6.79. 0.1800 , 24.5 c.c. of nitrogen at 17.5° and 766.5 mm. N=15.89. 0.1580 , 21.6 , , 17.5° , 752.7 mm. N=15.67. C_9H_{12}N_2O_4 requires C=59.97; H=6.66; N=15.59 per cent.
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When prepared by digesting the sodium compound of ethylic cyanacetate with ethylene dibromide at the ordinary pressure (p. 925), ethylic

abdicvanovalerate was obtained in the form of crystals which melt between 95° and 96°. These crystals were readily obtained in large, colourless, transparent prisms by recrystallisation from a mixture of alcohol and light petroleum (b. p. 60-80°), and had all the appearance of a pure substance. Repeated recrystallisation from this solvent did not raise the melting point above 96°; nevertheless, later investigation has shown that some impurity is not removed by this method. We were led to suspect the identity of this substance with that melting at 119.5° by the circumstance that exactly the same yield of adipic acid (80 per cent.) could be obtained from each. Accordingly, 5 grams of the substance melting at 95-96° were fractionally crystallised from absolute alcohol, when, after the third recrystallisation, the melting point reached 119.5°, and was not raised by further treatment in this manner. A portion thus obtained was mixed with a portion of the substance obtained under pressure; the melting point remained unchanged at 119.5°. In order to set the question of identity at rest, a complete analysis was made.

0.1491 gave 3278 CO₂ and 0.0900 H₂O. C=59.96; H=6.70. 0.1715 ,, 22.9 c.c. nitrogen at 19° and 762.5 mm. N=15.41. $C_0H_{12}N_9O_4$ requires C=59.97; H=6.66; N=15.59 per cent.

Ethylic aδ-dicyanovalerate is insoluble in cold water and light petroleum, appreciably soluble in boiling water, light petroleum, and cold. alcohol, and very soluble in boiling alcohol.

Conversion of Ethylic ab-Dicyanovalerate into Adipic Acid.

After several failures, the requisite conditions for this transformation were discovered, and a very good yield of adipic acid obtained. Three grams of the cyano-ethereal salt were treated with the calculated quantity of cold methyl alcoholic potash needed to hydrolyse the COOC. H. group. The alcohol was then evaporated off, and the residue boiled in a reflux apparatus with concentrated aqueous potash until ammonia ceased to be given off, which is the case in about two hours. Finally, the liquid was mixed with excess of 30 per cent, sulphuric acid, boiled for thirty minutes, and then set aside to crystallise. About 1.5 grams of an acid crystallised out, and another half gram was obtained by saturating the liquid with ammonium sulphate and extracting with ether. The acid, which is nearly colourless, melts at 148.5-149°; it is readily purified by crystallisation from hot water with the aid of animal charcoal, and is thus obtained in the form of colourless, lustrous plates melting at 149-149.5°. The samples for analysis were dried at 120°.

I, Acid obtained from ethylic $a\delta$ -dicyanovalerate prepared under pressure.

0.1749 yielded 0.3186 CO₂ and 0.1127 H₂O. C = 49.68; H = 7.09.

II, Acid obtained from ethylic a δ -dicyanovalerate prepared at the ordinary pressure:

0.1716 gave 0.3103 CO₂ and 0.1067 H₂O. C = 49.31; H = 6.90. $C_6H_{10}O_4$ requires C = 49.31; H = 6.85 per cent.

Specimens of the two acids were crystallised from concentrated nitric acid, and the aqueous solutions, on testing qualitatively, gave the characteristic reactions of adipic acid.

It should be mentioned that several attempts were made to prepare a dicyanovaleric acid from its ethereal salt by hydrolysis with cold methyl alcoholic potash, but without success.

Action of Trimethylene Dibromide on Ethylic Sodiocyanacetate. Formation of Ethylic Cyanotetramethylenecarboxylate, $CH_2 \cdot CH_2$ of $CH_2 \cdot CCOO_2H_5$.

The method of preparation is exactly analogous to that followed in the case of the corresponding trimethylene compound. The reaction is, however, more vigorous in the present instance, and some care is needed to prevent considerable loss of substance caused by the reacting mixture being thrown out of both flask and reflux condenser. By regulating the temperature carefully and shaking continuously, the reaction may be made to proceed evenly and with no violence. The isolation and purification of the product are conducted exactly as in the case of the trimethylene compound, and the oil boiling at 213—214° under 766 mm, pressure gave the following numbers on analysis:

0.2014 gave 0.4327 CO₂ and 0.1276 H₂O. C = 58.59; H = 7.04. 0.2038 yielded 16.5 c.c. nitrogen at 18.5° and 765 mm. N = 9.39. $C_8H_{11}NO_2$ requires C = 62.72; H = 7.19; N = 9.14 per cent.

The analytical numbers show that the liquid is not pure ethylic cyanotetramethylene carboxylate, but still contains ethylic cyanacetate.

 $\begin{tabular}{lll} Cyanotetramethylenecarboxylic Acid, & CH_2 \cdot CH_2 \\ CH_2 \cdot C(CN) \cdot COOH. \\ \end{tabular}$

The method of preparation differs in no respect from that of the corresponding trimethylene compound. The acid, which melts at 69—70°, is left as an oil by the evaporation of its concentrated ethereal solution, and only solidifies to a mass of colourless prisms after some

time. These are dried on a porous plate and recrystallised from pure carbon bisulphide containing a few drops of ether. In this way, magnificent, long, silky needles are obtained.

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0.2540 gave 0.5343 CO<sub>2</sub> and 0.1366 H<sub>2</sub>O. C=57.37; H=5.97. 0.2090 , 20.5 c.c. nitrogen at 17° and 748 mm. N=11.20. C_6H_7NO_2 requires C=57.58; H=5.59; N=11.22 per cent.
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Cyanotetramethylenecarboxylic acid may be sublimed unchanged if a small quantity be heated just above its melting point for some time, but the temperature must not be allowed to reach 160°, as at this point decomposition into cyanotetramethylene and carbon dioxide takes place. It is soluble in water, ether, chloroform, benzene, and acetone at the ordinary temperature, and in warm, but not in cold, carbon disulphide. A neutral solution of the ammonium salt in water, when treated with aqueous ferric chloride, behaves in a similar manner to that already described in the case of the corresponding trimethylene compound. The silver and barium salts of cyanotetramethylenecarboxylic acid were prepared in the same way as, and exhibit complete analogy to, the salts of the corresponding trimethylene acid.

Analysis of silver salt.

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0·1106 gave 0·0516 Ag. Ag = 46.65.
0·1787 , 0·0839 Ag. Ag = 46.95.
C_6H_6NO_2Ag requires Ag = 46.53 per cent.
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Analysis of the barium salt (dried at 140°).

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0.1964 gave 0.1168 BaSO<sub>4</sub>. Ba = 34.93.
0.2282 ,, 0.1349 BaSO<sub>4</sub>. Ba = 34.75.
(C_8H_8NO_9)_9Ba + \frac{1}{2}H_9O requires Ba = 34.77 per cent.
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Conversion of Cyanotetramethylenecarboxylic Acid into Tetramethylenedicarboxylic Acid.

This change is most readily effected by means of boiling concentrated aqueous potash, and the method of procedure is exactly the same as that described in detail in the case of the corresponding trimethylene derivative. In this way, an acid was obtained crystallising in colourless prisms which melted at 157°, and showed all the characteristic properties of tetramethylenedicarboxylic acid (m. p. 156°); it was dried at 120°, and was analysed with the following results:

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0.1721 gave 0.3188 CO<sub>2</sub> and 0.0883 H<sub>2</sub>O. C=50.52; H=5.70. C_6H_8O_4 requires C=50.00; H=5.55 per cent.
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The characteristic lead salt was prepared and analysed, after being dried in the air for 3 days.

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0.2548 yielded 0.2107 PbSO₄. Pb=56.43. 0.2745 lost 0.014 H₂O at 140°. H₂O=5.10. $C_6H_6O_4Pb+H_2O$ requires Pb=56.33; H₂O=4.91 per cent.

After being dried in a vacuum for 3 days,

0.4035 yielded 0.3507 PbSO₄. Pb = 59.33. 0.2846 , 0.2460 PbSO₄. Pb = 59.00. $C_6H_6O_4$ Pb requires Pb = 59.24 per cent.

There is a slight discrepancy between these results and those given in the earlier description of this salt (Perkin, Trans., 1887, 51, 8). It is there stated that the salt dried in a vacuum still contains $1H_2O$, but this is not the case, as is shown by the fact that a specimen of the lead salt prepared from tetramethylenedicarboxylic acid, obtained with the aid of ethylic malonate, after drying for 3 days in a vacuum, gave the following result on analysis:

0.2438 gave 0.2121 PbSO₄. Pb = 59.35. PbC₆H₆O₄ requires Pb = 59.24 per cent.

As the salts made from the two specimens of the acid resemble one another in every respect, and especially in their characteristic property of passing from the amorphous to the crystalline state on standing for a short time, or more quickly still on shaking, no doubt can exist as to their identity. Each salt, when dried in the air, contains $1\rm{H}_2\rm{O}$, but this is given up, either on heating to 140° or on standing in a vacuum.

$Cyanotetramethylene, \begin{array}{l} \mathbf{CH_2 \cdot CH_2} \\ \mathbf{CH_2 \cdot CH \cdot CN} \end{array}$

In order to prepare this interesting substance, 12 grams of cyanotetramethylenecarboxylic acid were distilled in portions of 6 grams at a time from a small retort heated in a bath of fusible metal. Carbon dioxide is given off very readily from 160° upwards, and the whole of the liquid (7.8 grams) distilled over below 190°. On redistilling the oil, it was found that the carbon dioxide had not been completely split off in one distillation, but after two more fractionations, about 5—5.5 grams of a liquid were obtained, boiling constantly at 148—149° under 760 mm. pressure.

0.1980 gave 0.5344 CO₂ and 0.1591 H₂O. C = 73.60; H = 8.92. 0.2301 ,, 34.6 c.c. nitrogen at 19.5° and 753.5 mm. N = 17.09. C_5H_7N requires C = 74.03; H = 8.64; N = 17.32 per cent.

The yield of cyanotetramethylene obtained by this reaction is at least 70 per cent. of the theoretical; it is a colourless, very mobile liquid,

has a pleasant odour, and is hydrolysed almost quantitatively by boiling concentrated aqueous potash to the corresponding tetramethylene-monocarboxylic acid, $CH_2 \cdot CH_2$ monocarboxylic acid, $CH_2 \cdot CH_2 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_3 \cdot CH_$

4.3 grams of cyanotetramethylene were boiled with 6 grams of potash dissolved in 20 c.c. of water for 6—7 hours in a reflux apparatus. When the evolution of ammonia had ceased, the liquid was allowed to cool, and then acidified with dilute sulphuric acid; the colourless oil which separated was extracted with ether in the usual way, and, after drying over anhydrous sodium sulphate and distilling off the ether, the residual liquid, on fractionation, passed over between 190° and 193°. This was again distilled, and the fraction 191—192° analysed.

0.2842 gave 0.6234 CO₂ and 0.2060 H₂O. C=59.82; H=8.05. $C_5H_8O_2$ requires C=60.00; H=8.00 per cent.

The characteristic calcium salt of this acid was prepared; it is very soluble in water, and crystallises from very concentrated solutions in silky needles.

Preparation of Pimelic Acid from the Bye-product of the Reaction between Trimethylene Dibromide and Ethylic Sodiocyanacetate.

The thick oil, which is left in the steam distillation flask, after distilling off the ethylic cyanacetate and cyanotetramethylenecarboxylate, and does not solidify on cooling, probably consists of diethylic aa₁-dicyanopimelate,

COOC, H5 · CH(CN) · CH6 · CH6 · CH(CN) · COOC, H5. It was extracted with ether, the ethereal solution dried over calcium chloride, and the ether distilled off; the residual oil was then boiled for about 20 hours in a reflux apparatus with concentrated aqueous potash. At the end of this time, complete hydrolysis had taken place, and the evolution of ammonia ceased. The liquid was acidified with sulphuric acid, and, after saturating with ammonium sulphate, extracted with ether; the ethereal solution was dried over anhydrous sodium sulphate and the ether distilled off, when an oil was left which was heated in a bath of fusible metal to 210° until the evolution of carbon dioxide had ceased. The dark coloured residue, which showed no signs of crystallising, was etherified by heating with 5 times its volume of absolute alcohol and one-fifth its volume of concentrated sulphuric acid for 2 hours in a reflux apparatus. The product was poured into water, extracted with ether, washed with sodium carbonate solution, dried, and the ether distilled off. On fractionating the residue at 40 mm. pressure, almost the

whole quantity distilled between 160° and 180°. This fraction was hydrolysed by boiling with methyl alcoholic potash, and after complete removal of the alcohol by evaporation with water, the residue was acidified and extracted with ether in the usual way. On allowing the ethereal solution to evaporate in a vacuum, an acid crystallised out which melted between 97° and 102°, and after recrystallising from benzene was finally obtained in a pure condition; it melted at 105°, and consisted of pure pimelic acid, as the following analysis shows:

0.1429 gave 0.2775 CO₂ and 0.1004 H₂O. C = 52.33; H = 7.80. $C_7H_{12}O_4$ requires C = 52.50; H = 7.50 per cent.

This acid gave a calcium salt, which separated from its cold, saturated solution on heating, a behaviour which is also shown by the ealcium salt of normal pimelic acid.

The authors wish to reserve the further examination of the substances described in this paper.

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XCI.—Influence of Substitution on Specific Rotation in the Bornylamine Series.

By MARTIN ONSLOW FORSTER, Ph.D., D.Sc.

ALTHOUGH recent years have witnessed the rapid multiplication of optically active substances, much remains to be learned respecting the influence of substitution on specific rotation before the guiding principles of the subject can be properly established. The theory propounded in 1890 almost simultaneously by Guye and Crum Brown, attracted considerable attention at the time, and has exerted a marked influence on the character of subsequent investigations. Some among the latter have seemed to afford confirmation of the theory, and more particularly of that deduction from it which predicts the occurrence of a point of maximum rotation in a homologous series (compare Frankland and MacGregor, Trans., 1893, 63, 1417, and 1894, 65, 756; Guye and Chavanne, Compt. rend., 1893, 116, 1454; 1894, 119, 906, and 1895, 120, 452). The general tendency of recent work, however, has been unfavourable to the original conception. Numerous cases of disagreement between results predicted and those found by experiment have led inevitably to a fuller recognition of influences exerted by the qualitative nature of substituent groups, influences foreshadowed by Crum Brown, and latterly

verified experimentally by other workers (compare Frankland and MacGregor, Trans., 1896, 69, 119, and Frankland, this vol., 347).

In the hope of gaining some information on this subject, I have prepared several alkyl derivatives of bornylamine, and determined their rotatory power in the liquid and dissolved states. Bornylamine was chosen because, in the first place, although numerous homologous series of optically active ethereal salts and alkyl oxides have been examined, the effect of replacing the aminic hydrogen of an optically active base by alkyl groups does not appear to have been studied. Secondly, it was recognised that a primary base, in which the aminogroup is attached to asymmetric carbon, offers two points of attack in one of the four groups causing asymmetry, instead of the one occurring in hydroxylic and carboxylic groups. An additional advantage which bornylamine offers may be found in the fact that it should give rise to one series of derivatives in which asymmetric nitrogen occurs in the trivalent condition, and a second containing quinquevalent asymmetric nitrogen.

Two objections to the choice of this substance, however, present themselves. In the first place, it contains two asymmetric carbon atoms besides that to which the amino-group is directly attached, and, secondly, this carbon atom forms part of a ring system, and consequently the "product of asymmetry" cannot be calculated by Guye's formula. On the other hand, active primary bases are not very numerous, and, in general, are not very readily obtained, whereas bornylamine can now be prepared without much difficulty (Forster, Trans., 1898, 73, 390).

At the outset of this investigation, much time was occupied in attempting to prepare methylbornylamine, and a suitable process for obtaining the compound was not discovered until the study of the other derivatives enumerated in this paper had been concluded. cause of the difficulty lies in the fact that the action which methylic iodide exerts on the primary base is sufficiently vigorous to give rise to the dimethyl derivative in a cold ethereal solution, a large proportion of bornylamine being precipitated from the liquid in the form of hydriodide. Even when the more usual method of heating the base with methylic iodide and alcoholic potash in a reflux apparatus is adopted, it is found that the methyl and dimethyl derivatives are produced in approximately equal quantities, along with a considerable amount of trimethylbornylammonium iodide. A fresh obstacle is encountered on isolating methylbornylamine from the basic mixture by conversion into the nitrosamine, inasmuch as this method cannot be relied upon to yield a base having the maximum rotation. misleading, in fact, is the result of using this process, that at one

time I regarded ethylbornylamine as having greater specific rotatory power than the lower homologue (Proc., 1899, 15, 71).

By having recourse to a method which avoids both direct methylation and treatment with nitrous acid, it is possible to obtain highly purified methylbornylamine without much loss of material. The procedure is as follows. Bornylamine is first condensed with benzaldehyde, yielding benzylidenebornylamine, which melts at 57°; this compound is then heated with methylic iodide, which converts it into an unstable methiodide, melting at 215°. On attempting to recrystallise this derivative from a solvent containing water, it is resolved almost quantitatively into benzaldehyde and methylbornylamine hydriodide, from which the base may be liberated in the usual way.

The remaining alkyl derivatives of bornylamine are readily obtained. The nitrosamine method of separating the secondary from the tertiary bases may be applied in the case of ethylbornylamine without impairing the specific rotatory power of the product. At this point the action of alkyl iodides sustains a sharp check; monalkyl bases are still obtained without difficulty, but no production of the corresponding dialkyl derivative occurs under ordinary conditions.

The following table summarises the information which has been gained respecting the rotatory power of bornylamine and its alkyl derivatives.

	[a] _D .	[M] _» .	[a], in benzene.	[M], in benzene.	[a], in alcohol.	[M] _p in alcohol.
Bornylamine	89·0 84·0 81·7	+161.6 168.8 178.5 163.8 170.7 113.1	+57·1° 95·9 90·3 87·1 81·1 80·3 59·6 62·6	+87.3 160.1 163.4 169.8 158.1 167.8 107.8 130.8	+46·2° 81·0 75·4 72·0 68·8 64·8 48·7 50·5	+70.7 135.8 136.4 140.4 123.4 135.4 88.1 105.5

From this it appears that the introduction of a single methyl group produces a striking increase of rotatory power. The second column of figures will show that a maximum in the molecular rotation occurs at the third term of the homologous alkylbornylamines, which form a series in this respect quite similar to those examined by Guye and Chavanne, Frankland and MacGregor, Tschúgaeff, and others. The first column indicates, however, that the specific rotatory power of these compounds undergoes a regular decline from the first member of the series; groups such as this, in which the maximum occurs at the first term, are not common, but the phenomenon has been observed

by Guye and Chavanne in the valeric series (Compt. rend., 1893, 116, 1454), by Purdie and Williamson in studying the ethereal salts of methoxy- and ethoxy-succinic acids (Trans., 1895, 67, 957), and by Frankland and MacGregor among the dibenzoylglycerates (Trans., 1896, 69, 118).

In view of the suggestion that the true optical behaviour of initial members of such series may be possibly masked by molecular association (Frankland, this vol., 347), the molecular volumes of the secondary bases, experimentally determined, are compared in the following table with the values calculated by Traube's method (Ber., 1895, 28, 2724).

	Density.	Mol. vol. calculated.	Mol. vol. experimental.
Methylbornylamine, C ₁₁ H ₂₁ N	A-0A1A /1A9\	185·7	183.7
Ethylbornylamine, C ₁₂ H ₂₂ N		201·8	201.9
Propylbornylamine, C ₁₂ H ₂₅ N		217·6	218.2
Butylbornylamine, C ₁₄ H ₂₇ N		233·4	234.3

Although the higher homologues are not associated, these data suggest the possibility that molecular association may occur to a slight extent in the case of the methyl derivative.

A more novel point presents itself on comparing the specific rotatory power of bornylamine and its monalkyl derivatives with that of the corresponding tertiary bases. Reverting to the table on p. 936, it will be noticed that the effect produced on the rotation of bornylamine by introducing a single alkyl radicle into the amino-group, compared with the result of replacing both atoms of hydrogen, is very considerable. If it can be shown that other groups of alkylated amines exhibit the same characteristic, the phenomenon should have some bearing on a discussion of the influence exerted by substitution upon rotatory power. For it will be recognised that, in the series under consideration, it is destruction of molecular symmetry, and not increase of mass, which produces the more marked effects on the optical activity. Thus, on comparing the specific rotatory power of ethylbornylamine and dimethylbornylamine with that of the primary base in benzene, it is found that although the radicle attached to asymmetric carbon undergoes in each instance a change in mass from 16 units to 44, the specific rotatory power is raised through only 2.5° in the one case, and through 33.2° in the other.

Bornylamine.

$$H$$
 $C_9H_{16}=0-N < H$
 $A = +57 \cdot 1^\circ$.

Dimethylbornylamine.
H

$$C_9H_{16}$$
—C-N $C_{CH_3}^{CH_3}$
[a]_D = +59.6°.

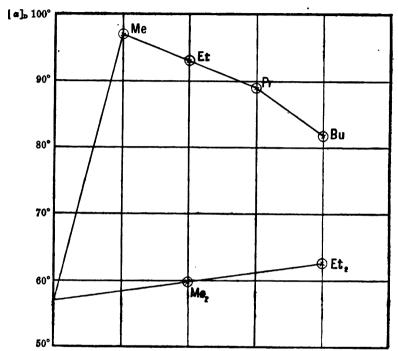
Ethylbornylamine.

H

$$C_9H_{16}$$
 $-C$
 $-N$
 $C_{2}H_{4}$

[a]_D = +90.3°.

Similarly, the change in mass from 16 units to 72, associated with the conversion of bornylamine into diethylbornylamine and butylbornylamine, is attended by an increase in specific rotatory power of 5.5° and 23.2° in the respective cases; the difference in this



Influence of Substitution on Specific Rotation in the Bornylamine Series.

The specific rotation of each monalkyl derivative in the liquid state is plotted on the upper curve; the values obtained with a dilute solution of the dialkyl derivatives in benzene are those represented in the lower.

instance, although considerable, is less striking, owing to the lower position in the curve occupied by butylbornylamine.

The fact that such a difference exists may not be due solely to mole cular distortion occasioned by the unsymmetrical disposition of the single alkyl group; it is possible that an asymmetric atom of nitrogen, even in the trivalent condition, may be inherently capable of at least modifying optical activity. With the object of studying this question, an attempt will be made to prepare unsymmetrical dialkylbornylamines, in order to compare their specific rotatory power with that of the bases under discussion.

It has become usual to represent the affinities of trivalent nitrogen

as if symmetrically disposed in one plane. From this point of view, it will be readily understood that the disposition of the nitrogen atom, relatively to asymmetric carbon, is seriously disturbed by replacement of a single hydrogen atom, whilst undergoing but slight modification when substitution of both occurs. It therefore became of interest to

compare the rotation of the derivatives, $C_{10}H_{17}\cdot NH\cdot CH_2$ and $C_{10}H_{17}\cdot NH\cdot CH_2$ X, in order to ascertain which differed the more widely from that of the compound $C_{10}H_{17}\cdot NH\cdot CH_2$.

In the case of the nitrobenzylbornylamines, the specific rotation of the ortho-derivative shows the greater divergence, which is even more striking among the hydrochlorides.

	[a] in benzene.	[M] _p in benzene.	[a] _D in alcohol.	[M] _p in alcohol.
Benzylbornylamine Orthonitrobenzylbornylamine Paranitrobenzylbornylamine Benzylbornylamine hydrochloride. Orthonitrobenzylbornylamine hydrochloride. Paranitrobenzylbornylamine hydrochloride.	77·9 —	+ 204·8 218·1 224·8 — —	+75.7° 61.2 66.6 35.8 113.2 20.8	+188.9 176.2 191.8 100.0 866.7 65.7

Such investigations are of less value than those which deal with replacement of hydrogen atoms in closer proximity to asymmetric Considerable attention has been recently paid, however, to the relationship between optical activity and position isomerism (compare Frankland and Wharton, Trans., 1896, 69, 1309; Frankland and McCrae, Trans., 1898, 73, 307, and Tschugaeff, Ber., 1898, 31, 1775). It has been shown that, in the case of methylic and ethylic tartrates, the greatest influence is exerted on rotation by the introduction of two paratoluyl groups, and the least by two orthotoluyl groups (Frankland and Wharton), but, as pointed out by Frankland and McCrae (loc. cit.), this relationship does not appear to be a general one; in fact, of the ten series quoted by these authors, six exhibit a relationship similar to that subsisting between benzylbornylamine and its nitro-derivatives, namely, closer approximation to the specific rotatory power of the original compound on the part of a para- than of an ortho-derivative. This is also true of the series comprising diethylic monobenzoyltartrate, diethylic monoparatoluyltartrate, and diethylic monorthotoluyltartrate, examined by Frankland and McCrae (loc. cit.), and of two series not mentioned by these investigators, namely, the hydroxybenzylidenefenchylamines and the methoxybenzylidenefenchylamines, described by Wallach and Binz (Annalm, 1893, 276, 315). The regularity is again noticeable in the series of menthylic athers studied by Tschügaeff (Ber., 1898, 31, 1778), but the converse holds among the methylic and ethylic salts of benzoylmalic and toluylmalic acids, as shown quite recently by Frankland and Wharton (this vol., 337), and also among the methylic and ethylic salts of dibenzoylglyceric and ditoluylglyceric acids (Frankland and Aston, this vol., 493). It follows that in twelve of the twenty-one cases which have been hitherto examined, the effect produced on specific rotatory power by substitution is greater in the ortho- than in the paraposition, a result from which it is scarcely possible to draw any definite conclusion.

The following table of benzoyl derivatives reveals the marked influence exerted on rotatory power by the qualitative nature of a substituent (compare Frankland and MacGregor, Trans., 1896, 69, 119).

	[a] _D ,	[M] _D .
Benzoylbornylamine	- 21 ·8°	- 55 9
Benzoylmethylbornylamine	65.5	177.5
Benzoylethylbornylamine	65·2	185.7
Benzoylpropylbornylamine	60.4	180.2

Whereas the benzyl group increases the specific rotation of bornylamine, in alcohol, by 29.5° , introduction of the benzoyl radicle changes a dextrorotation of 46.2° into a levorotation of 21.8° . The ethyl group increases the dextrorotation of the alcoholic base by 29.2° , whilst the formyl radicle, although of equal mass, converts it into a levorotation of 42.1° ; the propyl and acetyl groups exhibit a similar relationship. Moreover, the entrance of a single alkyl group into bornylamine and benzoylbornylamine is attended in each case by intensification of rotatory power.

In this connection, the series of bornylammonium iodides deserves notice. The hydriodides of the alkylbornylamines have higher specific rotation than the salt of the primary base, in other words, replacement of hydrogen in bornylamine hydriodide by a single alkyl group produces an increase in rotatory power; but the following table would seem to indicate that when an alkyl group replaces hydrogen of the ammonium group in members of this series, the optical activity, instead of increasing in the positive sense, actually becomes reduced to feeble laworotation.

	[α] _D .	[M] _p .
Bornylamine hydriodide	+16.0° -8.9 -3.8 -4.1 -3.1	+44.9 -12.6 -11.1 -14.4 -11.3

Numerous reasons already exist for regarding the two affinities satisfied by nitrogen on becoming quinquevalent as differing in character from the three which it exerts in the trivalent form. If the above relation extends to other groups of active ammonium compounds, it will afford another illustration of this principle.

Experimental.

Methylbornylamine, C₁₀H₁₇·NH·CH₈.

When an ethereal solution of methylic iodide is added to bornylamine dissolved in ice-cold, dry ether, a bulky precipitate of white needles quickly separates, and if removed after an interval of only a few minutes, is found to consist chiefly of bornylamine hydriodide. During the succeeding hours precipitation continues, but the appearance of the product changes, until leaflets separate in place of needles; if the liquid is filtered after six or seven days and then evaporated, dimethylbornylamine hydriodide is obtained. Intermediate fractions consist of bornylamine and methylbornylamine hydriodides in varying proportions.

From this it appears that methylic iodide acts very readily on bornylamine. The preparation of methylbornylamine in quantity is consequently a matter of some difficulty, because even in presence of alcoholic potash, methylic iodide yields the methyl and dimethyl bases in almost equal proportion, leaving a considerable quantity of the primary base unattacked. The following method was therefore adopted for the direct methylation of bornylamine.

Eighty grams of bornylamine hydrochloride, dissolved in 500 c.c. of alcohol, were treated with 45 grams of caustic soda dissolved in the minimum quantity of water; methylic iodide (30 grams) was added to the cold liquid, which, after an interval of 12 hours, was heated in a reflux apparatus and treated from time to time with small quantities of the iodide until altogether 80 grams had been employed. The product was then acidified with hydrochloric acid, freed from alcohol by means of a current of steam, then rendered strongly alkaline with caustic soda, and again distilled in an atmosphere of steam. The distillate was just dissolved in dilute hydrochloric

acid, heated with 30 grams of sodium nitrite on the water-bath until action ceased, and when cold, extracted with ether. The ethereal solution was dried with calcium chloride, evaporated, and the residue digested with three parts of concentrated hydrochloric acid at about 70°. In a few minutes, vigorous action took place, and when this had ceased, the liquid was diluted with 300 c.c. of water, cooled, and extracted with ether in order to remove products of the action of nitrous acid on the bornylamine which had escaped the influence of methylic iodide; the aqueous portion was made alkaline with caustic soda and distilled in a current of steam, yielding methylbornylamine as a limpid, colourless oil.

The base has a faint odour of piperidine, and is readily volatile in steam; it boils at 205° under 759 mm. pressure.

0.1607 gave 0.4618 CO₂ and 0.1834 H₂O. C = 78.37; H = 12.68. $C_{11}H_{21}N$ requires C = 79.00; H = 12.57 per cent.

A solution containing 0.4787 gram diluted with benzene to 25 c.c. at 15°, gave $a_D = 3^\circ$ 12.25′ as the mean of six readings in a 2 dcm. tube, whence $[a]_D = +83.7^\circ$; a solution in absolute alcohol, prepared in a similar manner, gave $[a]_D = +69.5^\circ$. As stated in the introductory portion of this paper, however, the values here recorded are too low.

The most satisfactory method of preparing methylbornylamine consists in treating the methiodide of benzylidenebornylamine with boiling ethylic acetate (undried), when benzaldehyde is eliminated, and the liquid deposits methylbornylamine hydriodide as it cools. The salt is recrystallised from boiling water until the specific rotatory power remains constant at $[a]_{\rm D} = +26.6^{\circ}$ for a 1 per cent. solution in absolute alcohol; it is then dissolved in hot water, made alkaline with caustic soda, and extracted with ether. The ethereal solution is afterwards dried with solid potash and evaporated.

Methylbornylamine is strongly dextrorotatory, giving $a_D = 175^{\circ}$ 50 in a 2 dcm. tube at 21°; the sp. gr. is 0.9075 at the same temperature, whence $[a]_D = +96.8^{\circ}$.

A solution containing 0.5172 gram diluted to 25 c.c. with benzene at 19° gave $a_D = 3^\circ$ 58' in a 2 dcm. tube, whence $[a]_D = +95.9^\circ$; a solution in absolute alcohol containing 0.5064 gram diluted to 25 c.c. at 23° gave $a_D = 3^\circ$ 17' in a 2 dcm. tube, whence $[a]_D = +81.0^\circ$.

The hydrochloride is not very soluble in cold alcohol, and separates slowly in transparent, prismatic needles infusible below 250°. A 2·4 per cent. solution in absolute alcohol gave [α]_D = +31·0°.

The hydriodide is freely soluble in boiling water, and crystallises in lustrous needles; it also separates from ethylic acetate in transparent needles.

0.1510 gave 0.1210 AgI. I = 43.30. $C_{11}H_{21}N,HI$ requires I = 43.05 per cent.

The salt has a definite melting point and fuses to a colourless liquid at 251°. A one per cent. solution in absolute alcohol has $[a]_D = +26.6^\circ$.

The platinochloride is immediately precipitated on adding alcoholic platinic chloride to a solution of the hydrochloride in dilute alcohol. It dissolves very sparingly in boiling alcohol, but is freely soluble on addition of hydrochloric acid, and crystallises in felted masses of long, silky, pale red needles; the salt melts and decomposes at 254°.

0.2101 (dried in desiccator) gave 0.0541 Pt. Pt = 25.75. 0.1835 ,, 0.0473 Pt. Pt = 25.77. $(C_{11}H_{21}N)_2H_2PtCl_6$ requires Pt = 26.14 per cent. $(C_{11}H_{21}N)_2H_2PtCl_6 + \frac{1}{2}H_2O$ requires Pt = 25.83 per cent.

The benzoyl derivative dissolves freely in hot alcohol, and crystallises in large, transparent, hemimorphic pyramids of monosymmetric habit; it melts at 127°.

0.1479 gave 0.4338 CO₂ and 0.1238 H₂O. C = 80.00; H = 9.30. $C_{18}H_{25}NO$ requires C = 79.70; H = 9.22 per cent.

A solution containing 0.4429 gram in 25 c.c. of absolute alcohol at 24° gave $a_D = -2^{\circ} 20'$ as the mean of six readings in a 2 dcm. tube, whence $[a]_D = -65.5^{\circ}$.

Methylbornylhydrazine, C₁₀H₁₇·N(CH₃)·NH₂, is obtained by reducing nitrosomethylbornylamine with zinc dust and glacial acetic acid. It is a colourless oil, having an ammoniacal, camphor-like odour, and boils at 190—195° under 752 mm. pressure. The base reduces an ammoniacal solution of silver nitrate almost immediately when warmed, and is also oxidised by boiling Fehling's solution. Methylbornylhydrazine causes an immediate precipitation of mercury in a cold, aqueous solution of mercury acetamide (compare Forster, Trans., 1898, 73, 783).

Although there can be little doubt that methylbornylhydrazine is really produced by the method indicated, crystalline derivatives of the base have not yet been obtained. When mixed with benzaldehyde, water quickly separates, and a viscous oil is produced which does not reduce ammoniacal silver nitrate; similarly, acetaldehyde acts vigorously on the hydrazine, but the product is of an uninviting character. Furthermore, an attempt to prepare the benzoyl derivative by the Schotten-Baumann method gave a semi-solid substance from which nothing could be isolated besides benzoylmethylbornylamine (m. p. $128-129^{\circ}$; $[\alpha]_{\rm p}=-64.5^{\circ}$; N=5.60 per cent.).

Dimethylbornylamine, $C_{10}H_{17} \cdot N(CH_8)_2$.

The mixture of bases obtained on heating 100 grams of bornylamine hydrochloride dissolved in 400 c.c. of alcohol with 50 grams of caustic soda and 80 grams of methylic iodide, was dissolved in dilute hydrochloric acid and heated with sodium nitrite in a reflux apparatus on the water-bath during half an hour. The nitroso-derivative of methylbornylamine, along with the products of the action of nitrous acid on the unmethylated base, was removed by distillation in a current of steam; the aqueous residue was then made alkaline with caustic soda, and once more distilled in steam.

Dimethylbornylamine is a limpid, colourless oil, having an odour which is distinctly basic, but less pronounced than that of the monalkyl base; it boils at 210—212° under 763 mm. pressure.

0.1330 gave 0.3903 CO₂ and 0.1524 H₂O. C=80.03; H=12.73. $C_{12}H_{23}N$ requires C=79.55; H=12.70 per cent.

The base is dextrorotatory, giving $a_D = 114^{\circ}$ 12' in a 2 dcm. tube at 16°; its specific gravity is 0.9123 at the same temperature, whence $[\alpha]_D = +62.5^{\circ}$.

A solution containing 0.3895 gram diluted to 25 c.c. with benzene at 10° gave $\alpha_D = 1^{\circ}$ 51.5' as the mean of ten readings in a 2 dcm. tube, whence $[\alpha]_D = +59.6^{\circ}$; a similarly prepared solution in absolute alcohol containing 0.6514 gram, gave $[\alpha]_D = +48.7^{\circ}$ at 23°.

Employing benzene as the solvent, a cryoscopic determination of the molecular weight of dimethylbornylamine was made. An examination of bornylamine was first carried out, in order to test the apparatus, and as a mean of four determinations the molecular weight was found to be 153.6 (calculated 153).

Grams of benzene.	Grams of base.	Grams of base in 100 grams of solvent.	Depression of freezing point.	Molecular weight deduced.
13:12	0.1048	0.795	0·262°	148-7
"	0.2608 0.8701	1 ·988 2 ·821	0.814 0.860	158·6 160·7

Molecular weight of dimethylbornylamine = 181.

The hydrochloride crystallises from alcohol in small, white needles, and does not melt below 300° ; a 1.7 per cent. solution in absolute alcohol has $[a]_{D} = +37.2^{\circ}$.

The platinochlorids crystallises from alcohol in two forms, (I) long, dark red needles, and (II) smaller, orange needles,

I. 0.1318 gave 0.0330 Pt. Pt = 25.04.

II. 0.2040 , 0.0515 Pt. Pt = 25.24.

 $(C_{12}H_{23}N)_2$, H_2 PtCl₆ requires Pt = 25·19 per cent.

Both forms melt and decompose at 230-231°.

Trimsthylbornylammonium Iodide, $C_{10}H_{17}\cdot N(CH_3)_3I$, prepared by heating bornylamine with methylic iodide ($3\frac{1}{2}$ mols.) and alcoholic soda, is sparingly soluble in cold water, and crystallises from the hot solution in magnificent, rectangular, transparent plates, infusible below 250° ; a 2.9 per cent. solution in absolute alcohol has $\lceil a \rceil_D = -3.9^\circ$.

0.1477 gave 0.1071 AgI. I = 39.18.

 $C_{18}H_{26}NI$ requires I = 39.32 per cent.

The chloride is highly deliquescent, and dissolves very readily in water, from which it crystallises in lustrous, white leaflets; a 4·1 percent. solution in water has $\begin{bmatrix} a \end{bmatrix}_D = -4\cdot4^\circ$.

The platinochloride crystallises from alcohol in highly lustrous, flat needles,

0.2243 gave 0.0548 Pt. Pt = 24.43.

 $(C_{18}H_{26}N)_2$, H_2 PtCl₆ requires Pt = 24.25 per cent.

The crystals are transparent in the mother liquor, becoming opaque on exposure to air; they melt and decompose at 242°.

Ethylbornylamine, C10H17 NH C2H5.

One hundred and twenty grams of bornylamine hydrochloride were dissolved in 750 c.c. of alcohol and treated with 75 grams of caustic potash dissolved in the minimum quantity of water; 75 grams of ethylic bromide were then added in small quantities at a time to the liquid, which was heated in a reflux apparatus on the water-bath during 8 hours. The basic product, which weighed 100 grams, was converted into the hydrochloride, which is not very readily soluble in water, particularly in presence of hydrochloric acid; a definite salt was therefore secured by recrystallising the mixture from dilute hydrochloric acid, and then from water, until a product of constant specific rotatory power was obtained. The base is a colourless oil, with a faint, fragrant odour; it boils at 215—216° under 758 mm. pressure.

0.1885 gave 0.5490 CO₂ and 0.2148 H₂O. C = 79.43; H = 12.66. $C_{12}H_{28}N$ requires C = 79.55; H = 12.70 per cent.

Ethylbornylamine is strongly dextrorotatory, giving $a_D = 166^{\circ}$ 23' in a 2 dcm. tube at 21°; the sp. gr. is 0.8947 at the same temperature, whence $[a]_D = +93.0^{\circ}$.

A solution containing 0.5077 gram diluted to 25 c.c. with benzene VOL. LXXV.

at 15°, gave $a_D = 3^\circ$ 40′ as the mean of five readings in a 2 dcm. tube, whence $[a]_D = +90.3^\circ$; a similarly prepared solution in absolute alcohol containing 0.6682 gram gave $a_D = 4^\circ$ 2′, corresponding to $[a]_D = +75.4^\circ$. The molecular weight, as determined in benzene, was found to be abnormal in almost the same degree as that of dimethyl bornylamine.

Grams of benzene.	Grams of base.	Grams of base in 100 grams of solvent,	Depression of freezing point.	Molecular weight deduced.
16-65	0.1088	0.6584	0.205°	156-1
"	0·2219 0·8800	1·3327 1·9820	0·405 0·608	161-2 161-0

Molecular weight of ethylbornylamine = 181.

The hydrochloride crystallises from water in white, lustrous leaflets, infusible below 250° ; a 1·3 per cent. solution in water has $[a]_{D} = +35^{\circ}6$

The hydriodide crystallises from water in thin, transparent plates a 2 per cent. solution in absolute alcohol has $[a]_n = +26.6^{\circ}$.

The nitrite is sparingly soluble in water and crystallises from boiling ethylic acetate in minute, lustrous needles, decomposing at 194°.

0.1410 gave 14.7 c.c. of moist nitrogen at 17° and 740 mm. N = 11.77. $C_{12}H_{28}N, HNO_3$ requires N = 12.28 per cent.

The platinochloride crystallises from alcohol in long, red, transparent prisms; it blackens at 220—230°, and melts and decomposes at 238°.

0.1514 gave 0.0384 Pt. Pt = 25.36. 0.2484 gave 0.0622 Pt. Pt = 25.04. $(C_{12}H_{23}N)_{2}H_{2}$ PtCl₆ requires Pt = 25.19 per cent.

The nitrosamine is a yellow oil, having a fragrant, camphor-like odour; it gives Liebermann's reaction, and decomposes when distilled under atmospheric pressure. Concentrated hydrochloric acid regenerates the secondary base when heated with the nitroso-derivative at the temperature of the water-bath; the base prepared in this way has the same specific rotatory power as a specimen derived from the recrystallised hydrochloride.

The acstyl derivative is a pale yellow oil which boils at 285—290° under a pressure of 765 mm.; it is slightly volatile in an atmosphere of steam, and is almost without odour. It is extremely difficult to regenerate the secondary base by the agency of hydrolytic agents (compare Wallach, Annalen, 1898, 300, 278).

The benzoyl derivative crystallises slowly from absolute alcohol in well-formed, transparent prisms and melts at 93-94°.

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0.1756 gave 8.5 c.c. of moist nitrogen at 20° and 764 mm. N = 5.56. $C_{19}H_{27}NO$ requires N = 4.91 per cent.

A solution containing 0.6903 gram in 25 c.c. of absolute alcohol at 21° gave $a_D = -3^\circ$ 36' as the mean of seven readings in a 2 dcm. tube, whence $[a]_D = -65.2^\circ$.

Dimethylethylbornylammonium Iodide, $C_{10}H_{17}\cdot N(CH_3)_2(C_3H_5)I$, prepared by heating ethylbornylamine with methylic iodide ($2\frac{1}{2}$ mols.) and alcoholic soda in a reflux apparatus, crystallises from water in minute, white needles and melts at 270° , when it decomposes.

0.2100 gave 0.1454 AgI. I = 37.41. $C_{14}H_{28}NI$ requires I = 37.69 per cent.

A 2 per cent. solution in absolute alcohol gave $[a]_D = -3.3^\circ$ at 18° .

Disthylbornylamine, $C_{10}H_{17}$ $N(C_2H_5)_2$.

The action of ethylic iodide differs from that of methylic iodide on bornylamine. Whereas the latter, even in cold ether, produces a certain amount of dimethylbornylamine, diethylbornylamine is obtained with some difficulty even under the influence of boiling alcoholic potash, whilst the iodide of the ammonium type, produced in large quantities when bornylamine is heated with methylic iodide and alcoholic soda, has not been hitherto obtained in the case of the higher homologue.

Fifty grams of bornylamine hydrochloride, dissolved in 300 c.c. of alcohol, were heated with 30 grams of caustic potash and 90 grams of ethylic iodide during several hours in a reflux apparatus. The mixture of bases obtained in this way was dissolved in excess of dilute sulphuric acid, and heated with 50 grams of sodium nitrite on the waterbath during one hour; after removing the nitrosamine with ether, the aqueous solution of diethylbornylamine sulphate was reduced to a small bulk on the water-bath and again extracted with ether in order to free it from a small quantity of nitrosamine which had separated during evaporation. The liquid was then treated with excess of caustic soda and distilled in steam. The base is a colourless oil with a faint, fragrant odour; it boils at 232—234° under a pressure of 750 mm.

0.1910 gave 0.5646 CO₂ and 0.2251 H₂O. C = 80.62; H = 13.10. $C_{14}H_{27}N$ requires C = 80.38; H = 12.92 per cent.

A solution containing 0.3991 gram, diluted to 25 c.c. with benzene at 15°, gave $a_D = 2^\circ$ 0' as the mean of five readings in a 2 dcm. tube, whence $[a]_D = +62.6^\circ$; a similarly prepared solution in absolute

alcohol containing 0.4952 gram gave $a_D = 2^{\circ} 0'$ as the mean of six readings at 22°, corresponding to $[a]_D = +50.5^{\circ}$.

The platinochloride crystallises slowly from cold alcohol in bright red, transparent prisms.

0.1958 gave 0.0465 Pt. Pt = 23.75. 0.2340 gave 0.0558 Pt. Pt = 23.84. $(C_{14}H_{27}N)_{g_1}H_{2}PtCl_{g}$ requires Pt = 23.48 per cent.

The salt melts and intumesces at 203°.

Propylbornylamins, $C_{10}H_{17}\cdot NH\cdot C_8H_7$.

Sixty grams of bornylamine hydrochloride dissolved in 400 c.c. of alcohol were heated with 60 grams of normal propylic iodide and the calculated amount of caustic soda in a reflux apparatus on the waterbath. On acidifying the product with hydrochloric acid and removing alcohol by distillation, a considerable precipitate of propylbornylamine hydriodide was obtained; this was recrystallised from boiling water and decomposed with alkali, the resulting base being then converted into the nitrosamine. The latter was hydrolysed by the action of three parts of concentrated hydrochloric acid at the temperature of the waterbath, and the salt, after being once washed with ether, was dissolved in water and rendered alkaline with soda. Propylbornylamine is a colourless, limpid oil having a faint basic odour; it boils at 234° under 769 mm. pressure.

0.1770 gave 0.5194 CO₂ and 0.2066 H₂O. C = 80.03; H = 12.97. $C_{18}H_{26}N$ requires C = 80.00; H = 12.82 per cent.

The base is strongly dextrorotatory, giving $a_D = 158^{\circ}$ 44' in a 2 dcm. tube at 18°; its sp. gr. is 0.8919 at the same temperature, whence $[a]_D = +89.0^{\circ}$.

A solution containing 0.6051 gram diluted to 25 c.c. with benzene at 15°, gave $a_D = 4^{\circ}$ 13' as the mean of seven readings in a 2 dcm. tube, whence $[a]_D = +87\cdot1^{\circ}$; a similarly prepared solution in absolute alcohol containing 0.5210 gram gave $a_D = 3^{\circ}$ 0' as the mean of six readings at 16°, corresponding to $[a]_D = +72\cdot0^{\circ}$.

The hydrochloride forms snow-white scales; a 2 per cent. solution in absolute alcohol gave $[a]_0 = +34.4^{\circ}$.

The hydriodide dissolves sparingly in cold water and crystallises in pale yellow, transparent prisms; a 1.7 per cent. solution in absolute alcohol gave $[a]_0 = +25.0^{\circ}$.

The platinochloride crystallises from alcohol containing hydrochloric acid in lustrous, red, prismatic needles; it blackens and intumesces at 231°.

0.2322 gave 0.0566 Pt. Pt = 24.37.

 $(C_{18}H_{26}N)_{s}$, $H_{2}PtCl_{6}$ requires Pt = 24.31 per cent.

The bensoyl derivative crystallises from dilute alcohol in white needles and melts at 85—86°.

0.1586 gave 0.4706 CO₂ and 0.1402 H₂O. C = 80.92; H = 9.82. $C_{20}H_{20}NO$ requires C = 80.27; H = 9.70 per cent.

A solution containing 0.4902 gram in 25 c.c. of absolute alcohol at 14° gave $a_D = -2^\circ$ 22' as the mean of eight readings in a 2 dcm. tube, whence $[a]_D = -60.3^\circ$.

Dimethylpropylammonium Iodide, $C_{10}H_{17}$ ·N(CH_8)₂(C_8H_7)I, was the result of an attempt to prepare methylpropylbornylamine, consequent on a complete failure to obtain dipropylbornylamine. Thirty grams of propylbornylamine were dissolved in alcohol and heated with 45 grams of methylic iodide and 12 grams of caustic soda in a reflux apparatus during several hours. On applying the nitrosamine method of separation, about one-third of the propylbornylamine employed was recovered unchanged, whilst the remainder had been converted into dimethylpropylbornylammonium iodide. This crystallises from water in aggregates of lustrous leaflets, melts with effervescence at 204—205°, and displays a marked tendency to form supersaturated solutions. It is sparingly soluble in aqueous caustic soda.

0.2143 gave 0.1432 AgI. I = 36.11. $C_{15}H_{50}NI$ requires I = 36.18 per cent.

A solution containing 0.5086 gram in 25 c.c. of absolute alcohol at 16° gave $\alpha_D = -10'$ as the mean of six readings in a 2 dcm. tube, whence $[\alpha]_D = -4.1^{\circ}$.

Isopropylbornylamine, C₁₀H₁₇·NH·C₃H₇^{\$}.

The conditions observed in preparing this substance were the same as those followed for the production of the isomeride, but it was found that a considerable proportion of bornylamine remained unchanged, as if isopropylic iodide were less vigorous in its action than the normal compound. The base is a colourless, limpid oil, having an odour which is fainter than that of the normal base; it boils at 223° under 769 mm. pressure.

0.1646 gave 0.4826 CO₂ and 0.1946 H_2O . C = 79.96; H = 13.14. $C_{18}H_{26}N$ requires C = 80.00; H = 12.82 per cent.

Examined in a 2 dcm. tube, isopropylbornylamine gave $a_D = 148^{\circ} 50$ at 14° ; the sp. gr. is 0.8861 at the same temperature, whence $[a]_D = +84.0^{\circ}$.

A solution containing 0.5008 gram diluted to 25 c.c. with benzene at 16° gave $a_D = 3^{\circ} 15'$ in a 2 dcm. tube, whence $[a]_D = +81 \cdot 1^{\circ}$; a

similarly prepared solution in absolute alcohol containing 0.5035 gram gave $a_0 = 2^{\circ}$ 33' at 16°, whence $[a]_0 = +63.3^{\circ}$.

The platinochloride dissolves very readily in alcohol, and separates slowly in red, transparent crystals.

0.2340 gave 0.0564 Pt. Pt = 24.10.

 $(C_{13}H_{25}N)_2$, H_2 PtCl₆ requires Pt = 24.31 per cent.

When heated in a capillary tube, the salt blackens at 210—220° and intumesces at about 240°.

Normal Butylbornylamins, C10H17 NH · C4H2.

Forty grams of bornylamine hydrochloride were dissolved in 300 c.c. of alcohol and heated with normal butylic iodide and the calculated quantity of caustic soda during several hours in a reflux apparatus. The usual operations of acidification, removal of alcohol, liberation of the base, and distillation in steam were then carried out, and the oily product, which appeared to be free from unchanged bornylamine, was dissolved in dilute sulphuric acid. On adding a concentrated, aqueous solution of sodium nitrite, a voluminous precipitate of white needles separated, changing to a pale yellow oil when heated on the water-bath; this product, the nitrosamine of butylbornylamine, solidified on cooling, and the crystals were therefore freed from oily products and heated with three parts of concentrated hydrochloric acid on the water-bath. This treatment rapidly converted the nitrosoderivative into the hydrochloride of the amine, which was then dissolved in water and made alkaline with caustic soda.

Butylbornylamine is a colourless, somewhat viscous oil with a marked basic odour; it boils at 249—251° under 760 mm. pressure.

0.1559 gave 0.4590 CO₂ and 0.1891 H₂O. C = 80.30; H = 13.47. $C_{14}H_{27}N$ requires C = 80.38; H = 12.92 per cent.

The base is strongly dextrorotatory, giving $a_D = 145^{\circ} 30'$ in a 2 dcm. tube at 15°; the sp. gr. is 0.8902 at the same temperature, whence $[a]_D = +81.7^{\circ}$.

A solution containing 0.4867 gram diluted to 25 c.c. with benzene at 16° gave $a_D = 3^\circ$ 7.5′ as the mean of eight concordant readings in a 2 dcm. tube, whence $[a]_D = +80.3^\circ$; a similarly prepared solution in absolute alcohol containing 0.4983 gram gave $a_D = 2^\circ$ 35′ at 16°; whence $[a]_D = +64.8^\circ$.

The hydrochloride separates from hot, aqueous solutions in the form of long, lustrous needles; a 2 per cent. solution in absolute alcohol gave $[a]_D = +32.7^{\circ}$.

The hydriodide is very sparingly soluble in water; a 2 per cent. solution in absolute alcohol gave $\lceil a \rceil_n = +23.8^\circ$.

The platinochloride, which separates slowly from an alcoholic solution in lustrous, red leaflets, melts and decomposes at 227°,

0.2102 gave 0.0496 Pt. Pt = 23.59, $(C_{14}H_{27}N)_2, H_2PtCl_6$ requires Pt = 23.48 per cent,

In the nitrite is scarcely soluble in cold water, and becomes dissociated when gently warmed with it; boiling ethylic acetate deposits it on cooling in highly lustrous, silky needles, which soften at about 195°, but have no definite melting point. The rotatory power of its solution in absolute alcohol indicates complete dissociation.

Dimethylbutylbornylammonium Iodide, $C_{10}H_{17}\cdot N(CH_8)_2(C_4H_9)I$, prepared by heating butylbornylamine with methylic iodide ($2\frac{1}{2}$ mols,) and alcoholic potash in a reflux apparatus, crystallises from water in long, silky, white needles and melts at 178°.

0.1980 gave 0.1262 AgI. I = 34.44, $C_{16}H_{52}NI$ requires I = 34.79 per cent.

A 2 per cent, solution in absolute alcohol gave $[a]_D = -3.1^\circ$,

Benzylbornylamine, C₁₀H₁₇·NH·CH₂·C₆H₅.

Fifty grams of bornylamine hydrochloride were dissolved in 300 c.c of alcohol and heated with 50 grams of benzylic chloride and the calculated quantity of caustic soda in a reflux apparatus during 12 hours; the product was acidified with 100 c.c. of concentrated hydrochloric acid and evaporated on the water-bath to remove alcohol, The benzylbornylamine hydrochloride obtained in this manner was crystallised from a large volume of boiling water and redissolved in sufficient water to yield a clear solution when cold; the salt was then precipitated by hydrochloric acid in two separate fractions, of which the first represented about three-quarters of the total amount. fraction, having a somewhat higher specific rotatory power than the second, was then triturated with concentrated alkali and extracted with ether; the ethereal solution was dried with solid potash and evaporated. The base is a colourless, highly refractive, somewhat viscous oil having a scarcely perceptible odour, and a slightly astringent taste; it boils at 313-315° under a pressure of 740 mm., and is not readily volatile in an atmosphere of steam.

0.1746 gave 0.5422 CO_2 and 0.1662 H_2O . C = 84.68; H = 10.57. $C_{17}H_{25}N$ requires C = 83.95; H = 10.28 per cent.

Benzylbornylamine resembles the alkylic bases in its high dextrorotation, giving $a_D = 161^{\circ} 30'$ in a 2 dcm. tube at 17°; the sp. gr. is 0.9818 at the same temperature, whence $[a]_D = +82.2^{\circ}$.

A solution containing 0.5025 gram, diluted to 25 c.c. with bensene at 14°, gave $a_D = 3^\circ$ 23′ as the mean of six readings in a 2 dcm. tube, whence $[a]_D = +84\cdot1^\circ$; a similarly prepared solution, containing 0.5571 gram in absolute alcohol at 20°, gave $a_D = 3^\circ$ 22.5′ as the mean of six readings in a 2 dcm. tube, whence $[a]_D = +75\cdot7^\circ$.

The hydrochlorids is sparingly soluble in cold water, and crystallises from hot solutions in lustrous needles, remaining unfused at 250° ; a 1.7 per cent. solution in absolute alcohol gave $[a]_{D} = +35.8^{\circ}$.

The platinochloride is sparingly soluble in hot alcohol, but dissolves more readily when hydrochloric acid is added to the liquid, from which it crystallises on cooling in beautiful, bright red, transparent needles.

0.2432 gave 0.0518 Pt, Pt = 21.30.

 $(C_{17}H_{25}N)_2, H_2PtCl_6$ requires Pt = 21.70 per cent.

The salt blackens and intumesces at 242°.

Orthonitrobenzylbornylamine, $C_{10}H_{17}\cdot NH\cdot CH_{2}\cdot C_{6}H_{4}\cdot NO_{2}$.

Forty grams of bornylamine hydrochloride, dissolved in 300 c.c. of alcohol, were heated with 46 grams of orthonitrobenzylic chloride and the calculated quantity of caustic soda in a reflux apparatus during 8 hours; on filtering the cold solution from sodium chloride and removing alcohol by evaporation, a dark red, syrupy residue was obtained which immediately solidified when treated with dilute hydrochloric acid. The crude salt had a penetrating benzylic odour, which it retained after being recrystallised twice from water, but on recrystallising the substance once more from boiling water and washing the product with other on porous earthenware, highly lustrous, colourless, odourless scales were obtained. This treatment raised the specific rotatory power from 109.0° to 113.2°, at which point it remained constant; the salt was therefore dissolved in hot water and treated with excess of caustic soda, which precipitated the base as a pale yellow oil, rapidly solidifying in hard crystals as the liquid cooled. The product was boiled with a small quantity of hot alcohol and rapidly cooled; on recrystallisation from hot, dilute alcohol, orthonitrobenzylbornylamine was obtained in minute, pale yellow, transparent prisms, slowly becoming dark brown on exposure to light.

0.1757 gave 0.4601 CO₂ and 0.1356 H₂O. C = 71.42; H = 8.57. $C_{17}H_{24}N_{2}O_{2}$ requires C = 70.83; H = 8.33 per cent.

The base melts at 39—40°, and although so easily fusible, solidifies with great readiness; from dilute solutions, it separates slowly in long, flat needles. It dissolves readily in benzene, forming a canary-yellow

liquid, an equally concentrated (2 per cent.) solution of paranitrobenzylbornylamine being practically colourless.

A solution containing 0.5082 gram in 25 c.c. of benzene at 15° gave $[\alpha]_D = 3^\circ$ 0.5′ as the mean of ten readings in a 2 dcm. tube, whence $[\alpha]_D = +74.0^\circ$; a solution of 0.5068 gram in 25 c.c. of absolute alcohol at 22° gave $\alpha_D = 2^\circ$ 29′, corresponding to $[\alpha]_D = +61.2^\circ$.

The hydrochloride forms highly lustrous, colourless scales, and has an intensely bitter taste; a 2 per cent. solution gave $[\alpha]_D = +113 \cdot 2^\circ$.

The platinochloride crystallises from alcohol containing hydrochloric acid in slender, highly lustrous, pale red needles.

0.1910 gave 0.0371 Pt. Pt = 19.42. $(C_{17}H_{24}N_2O_2)_pH_2PtCl_6$ requires Pt = 19.71 per cent.

The salt blackens and intumesces at 235°.

Paranitrobenzylbornylamine, $C_{10}H_{17}\cdot NH\cdot CH_{2}\cdot C_{6}H_{4}\cdot NO_{2}$.

The paranitrobenzyl derivative was prepared by the same method as that used for producing the ortho-compound, paranitrobenzylic chloride being substituted for the ortho-derivative. The dark brown residue obtained on evaporating the filtered alcoholic liquid was treated with dilute hydrochloric acid, the product being recrystallised twice from boiling water, and finally washed with ether on porous earthenware. On adding caustic soda to a boiling, aqueous solution of the salt, paranitrobenzylbornylamine was precipitated as a heavy, pale yellow, viscous oil which solidified on agitation in cold water; it was boiled with a quantity of alcohol insufficient to completely dissolve the fused base, then rapidly cooled, and recrystallised from hot alcohol, in which it is less readily soluble than the ortho-compound. It forms long, slender, lustrous needles which change into transparent, sulphuryellow prisms; the substance melts at 60—61°.

0.1583 gave 0.4129 CO₂ and 0.1245 H_2O . C = 71.13; H = 8.73. $C_{17}H_{24}N_2O_2$ requires C = 70.83; H = 8.33 per cent.

A solution containing 0.5082 gram in 25 c.c. of benzene at 15° gave $a_D = 3^\circ 10'$ as the mean of six readings in a 2 dcm. tube, whence $[a]_D = +77.9^\circ$; a solution of 0.5037 gram in 25 c.c. of absolute alcohol at 22° gave $a_D = 2^\circ 41'$, corresponding to $[a]_D = +66.6^\circ$.

The hydrochloride forms highly lustrous, colourless leaflets and does not melt below 250°; a 2 per cent. solution in absolute alcohol gave $[a]_0 = +20.3^{\circ}$.

The platinochloride crystallises from alcohol containing a large proportion of hydrochloric acid, in lustrous, red, transparent prisms.

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0.1829 gave 0.0356 Pt. Pt = 19.46. $(C_{17}H_{24}N_2O_2)_2, H_2PtCl_6 \text{ requires Pt} = 19.71 \text{ per cent.}$

The salt blackens and intumesces at 234°.

A subsequent communication will deal with the condensation products of bornylamine with aromatic aldehydes.

ROYAL COLLEGE OF SCIENCE, LONDON, SOUTH KENSINGTON, S.W.

XCII.—Studies of the Acids of the Acetylene Series.

By SIEGFRIED RUHEMANN and ALFRED V. CUNNINGTON.

In our last communication (this vol., p. 778), we showed that the action of the ethylic salts of acetoacetic and benzoylacetic acids on ethylic acetylenedicarboxylate differs from that of these ketonic compounds on ethylic phenylpropiolate, inasmuch as, instead of α -pyrone derivatives, ethereal salts are formed which most probably belong to the trimethylene series. This fact induced us to study the behaviour of ethylic phenylpropiolate and ethylic acetylenedicarboxylate towards other substances, in order to ascertain whether similar differences occur. First of all, their interaction with bases was submitted to a closer study in order that we might examine whether the addition is accompanied by the formation of cyclic compounds.

One of us and K. C. Browning (Trans., 1898, 73, 123) observed that the ethylic salts of unsaturated acids form additive products with piperidine, and that this base unites most readily with ethylic phenylpropiolate. It is noteworthy that diethylamine does not seem to combine with this salt at the ordinary temperature, and that it is necessary to heat the mixture at 100° in order to effect the union. With ethylic acetylenedicarboxylate, on the other hand, both bases unite most violently, and yield the corresponding additive compounds.

The ethereal salts of acetylenedicarboxylic and phenylpropiolic acids also react with other bases, such as hydroxylamine, urea, and benzamidine. Up to the present, we have completed the study of the behaviour of these substances towards ethylic phenylpropiolate and find that a cyclic compound is formed only with benzamidine. The constitution of this product, as shown below, has to be represented by one of the formulæ:

It stands, therefore, in a close relation to glyoxaline, and may be called benzalphenylglyoxalidone.

This paper also contains an account of the products formed by the union of bromine with the ethylic salts of phenylpropiolic and acetylenedicarboxylic acids. This study was undertaken with the object of substituting the group 'OH(COOC₂H₅)₂ of ethylic malonate for the bromine atoms in these compounds, and transforming the ethereal salts, which we expected to obtain, into pyridine derivatives. We find, however, that both bromine atoms are so fixed in the molecule of ethylic dibromocinnamate, that, on boiling the salt with concentrated caustic potash, hydrolysis only takes place, and two stereoisomeric dibromocinnamic acids, previously obtained by Roser and Haselhoff (Annalen, 1888, 247, 139), are formed.

The ethylic salt of the dibromo-acid shows the same degree of stability towards ethylic sodiomalonate, and is not altered even on heating the mixture in the presence of alcohol at 110°. This result differs most markedly from that arrived at by G. Pum (Monatch., 1889, 9, 446) in examining the action of ethylic sodiomalonate on ethylic dibromomaleate. According to him, the two compounds readily formed an ethereal salt, which he considered to be ethylic dimalonylmaleate, $COOC_2H_5 \cdot C \cdot CH(COOC_2H_5)_2$ This substance, he stated, yielded on COOC,H,·C·CH(COOC,H,), hydrolysis the corresponding hexacarboxylic acid, which, when heated, lost 2 mols. of carbonic anhydride and was transformed into the tetracarboxylic acid, diglycolylmaleic acid, of the formula COOH.C.CH..COOH COOH.C.CH..COOH.

This remarkable difference in the behaviour of the ethylic salts of dibromocinnamic and dibromomaleic acids induced us to test the correctness of Pum's observation. Moreover, a repetition of his experiments appeared to us advisable, because the ethereal salt which he used was impure, containing 4 per cent, less bromine than the calculated quantity. We find that pure ethylic dibromomaleate is certainly much less stable than ethylic dibromocinnamate; it can be hydrolysed by warming with caustic potash, but readily loses almost all its bromine on treatment with ethylic sodiomalonate. solid, however, which results, and which-Pum regarded as ethylic dimalonylmaleate, does not melt at 75°, but at 76°, and is nothing but ethylic ethanetetracarboxylate, the reaction taking place according to the equation:

$$\begin{aligned} \text{COOC}_2\mathbf{H}_5 \cdot \text{CBr} \cdot \text{COOC}_2\mathbf{H}_5 + 2\text{CHNa}(\text{COOC}_2\mathbf{H}_5)_2 &= \\ 2\text{NaBr} + \text{COOC}_2\mathbf{H}_5 \cdot \text{C} : \text{C} \cdot \text{COOC}_2\mathbf{H}_5 + \frac{\text{CH}(\text{COOC}_2\mathbf{H}_5)_2}{\text{CH}(\text{COOC}_2\mathbf{H}_5)_2}. \end{aligned}$$

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Ethylic acetylenedicarboxylate, which figures in this equation, unites almost completely, however, with ethylic malonate and forms ethylic propenetetracarboxylate, COOC₂H₅·CH·C(COOC₂H₅)·CH(COOC₂H₅)₂, which has been described by Michael (*J. pr. Chem.*, 1894, [ii],49, 20). The behaviour of ethylic dibromomaleate towards ethylic sodiomalonate is therefore similar to that of the ethereal salts of bromomalonic acid and its homologues (Ruhemann, *Ber.*, 1893, 26, 2356), and especially to that of ethylic dibromotricarballylate (Ruhemann and Allhusen, Trans., 1894, 65, 14).

In the light of our experiments, there cannot be any doubt as to the nature of the substances which Pum obtained from his so-called ethylic dimalonylmaleate. The acid which is formed from it on hydrolysis is ethenyltricarboxylic acid, COOH·CH₂·CH(COOH)₂, and his diglycolylmaleic acid is succinic acid.

The properties of the compounds as described by Pum do not essentially differ from those which are characteristic of ethylic ethanetetracarboxylate and the products of its decomposition. The differences in the percentage compositions are not very considerable, although in most cases they lie far beyond the limit of experimental error.

EXPERIMENTAL.

Ethylic Diethylamidocinnamate, $COOC_2H_5 \cdot CH: C(C_6H_5) \cdot N(C_2H_5)_2$.

Diethylamine, as stated above, does not unite with ethylic phenyl-propiolate so readily as piperidine, no heat being developed on mixing the two compounds. Combination, however, occurs on heating the mixture at 100° in a sealed tube, and it is complete after 6—8 hours. The substance formed is a yellowish oil which boils at 188° under 14 mm. pressure, and has a sp. gr. 1.038 at 19°/19°.

0.2080 gave 0.5540 CO₂ and 0.1582 H_2O . C = 72.64; H = 8.45. $C_{15}H_{21}NO_2$ requires C = 72.87; H = 8.50 per cent.

This compound, like those of piperidine with unsaturated acids (loc. cit.), has basic properties and forms a deliquescent hydrochloride.

I. Action of Piperidine and Diethylamine on Ethylic Acetylenedicarboxylate.

The action of these bases on the ethereal salt is accompanied by so great a development of heat that it is necessary to use ether as a diluent.

Ethylic Piperidylmaleate, $COOC_2H_5 \cdot CH^*: C(C_5NH_{10}) \cdot COOC_2H_5$.—On gradually adding the ethereal solution of piperidine to ethylic acetylene-dicarboxylate previously dissolved in ether, a green coloration is at

first produced, which afterwards changes to yellow. The yellowish oil which remains after removal of the ether boils at 210° under 16 mm. pressure, and has a sp. gr. 1.0920 at 26°/26°. On analysis, the following numbers were obtained:

0.2248 gave 0.5035 CO_2 and 0.1720 H_2O . C=61.08; H=8.50. $C_{13}H_{21}NO_4$ requires C=61.17; H=8.23 per cent.

Ethylic Diethylamidomaleate, $COOC_2H_5 \cdot CH \cdot C(COOC_2H_5) \cdot N(C_2H_5)_2$, prepared in a similar manner, is a yellowish oil which boils at 180° under 13 mm. pressure, has a sp. gr. $1\cdot052$ at $25^\circ/25^\circ$, and, on passing hydrochloric acid into its solution in dry ether, yields a hydrochloride which is exceedingly soluble in water. The oil was analysed with these results:

0.1981 gave 0.4315 CO₂ and 0.1565 H_2O . C = 59.40; H = 8.77. $C_{12}H_{21}NO_4$ requires C = 59.25; H = 8.64 per cent.

II. Action of Hydroxylamins, Urea, and Benzamidins on Ethylic Phenylpropiolats.

As mentioned in the introduction, our hope of arriving at cyclic compounds by the interaction of the above bases with ethylic phenyl-propiolate has been realised only in the case of benzamidine. Hydroxylamine and urea do not form additive compounds, but yield respectively the hydroxamic acid and the ureide of the unsaturated acid.

Phenylpropiolohydroxamic Acid, C,H,C:C·C(NOH)·OH.

This acid is obtained by mixing alcoholic solutions of calculated quantities of sodium ethoxide and hydroxylamine hydrochloride and gradually adding ethylic phenylpropiolate to the mixture. After standing for a day, the alcohol is evaporated and a yellowish solid remains which readily dissolves in water. On acidifying the solution with hydrochloric acid, the hydroxamic acid is precipitated; it dissolves readily in alcohol but with great difficulty in boiling water, from which it crystallises in almost colourless needles melting at 168—169°. On analysis, the following results were obtained:

0.2265 gave 0.5580 CO₂ and 0.0915 H₂O. C=67.18; H=4.48. 0.2955 ,, 22.5 c.c. of moist nitrogen at 20° and 770 mm. N=8.82. C₂H₇NO₂ requires C=67.08; H=4.34; N=8.70 per cent.

The substance is isomeric with phenylisoxazolone, which we expected to obtain in the above reaction. Its alcoholic solution gives, with ferric chloride, a red precipitate which dissolves in alcohol, producing a deep red solution.

The barium salt is precipitated when barium chloride is added to a solution of phenylpropiolohydroxamic acid in ammonia. It crystallises from boiling water in colourless plates of the composition $(C_9H_6NO_2)_2Ba + 2H_9O$.

0.2955 of the salt, dried in air, lost 0.0217 H_2O at 110°. $H_2O = 7.34$; calculated = 7.30 per cent.

0.2600, dried at 110°, gave 0.1320 BaSO₄. Ba = 29.85. $(C_0H_6NO_3)_2$ Ba requires Ba = 29.98 per cent.

The silver salt is formed as a gelatinous precipitate on mixing alcoholic solutions of the acid and silver nitrate. Before analysis, it was dried at 100°.

0.2482 left, on ignition, 0.0996 Ag. Ag = 40.12. $C_9H_6NO_2Ag$ requires Ag = 40.29 per cent.

The methylic salt, obtained by digesting the silver salt with an excess of methylic iodide for 3 hours on the water-bath and extracting the product with methylic alcohol, crystallises from dilute alcohol in colourless needles which dissolve in ether with great difficulty and melt at 72°.

0.2490 gave 17.5 c.c. moist nitrogen at 20° and 763 mm. N = 8.07. $C_9H_6NO_2$ CH₃ requires N = 8.0 per cent.

Ureide of Phenylpropiolic Acid, C6H5 C: CO NH CO NH2.

When ethylic phenylpropiolate, dissolved in dry ether or alcohol, is mixed with urea and sodium ethoxide in molecular proportion, heat is evolved and the whole becomes yellow. After standing for a day, the yellow precipitate is collected and washed with ether. It is readily soluble in water, and on the addition of dilute sulphuric acid to the solution a solid separates which dissolves in boiling water or alcohol and crystallises in faintly yellow needles melting at 220°.

0.1410 gave 0.3300 CO₂ and 0.0570 H₂O. C = 63.82; H = 4.49. 0.2236 ,, 28.5 c.c. nitrogen at 15° and 765 mm. N = 15.01. $C_{10}H_2N_3O_2$ requires C = 63.81; H = 4.25; N = 14.89 per cent.

This substance has acidic properties, dissolves freely in caustic potash, and is precipitated unchanged by hydrochloric acid. It dissolves in ammonia on warming, and this solution yields, with silver nitrate, a yellowish silver compound, which gave, on analysis, the following result:

0.2903 left, on ignition, 0.1068 Ag. Ag = 36.78. $C_{10}H_7N_2O_2Ag$ requires Ag = 36.61 per cent.

Benzalphenylglyoxalidons.

This cyclic compound is produced on mixing absolute alcoholic solutions of sodium ethoxide (2 mols.) and benzamidine hydrochloride (1 mol.) with ethylic phenylpropiolate (1 mol.). The mixture becomes yellow and sets to a semi-solid mass, which, after standing for a day, is collected and washed with ether. The product dissolves in water with the greatest ease, and the solution yields, with hydrochloric acid, a yellow precipitate which is sparingly soluble in ether or alcohol, but readily so in boiling glacial acetic acid, and crystallises in yellow needles melting at 274° to a red liquid. On analysis, the compound gave the following numbers:

0.2075 gave 0.5895 CO₂ and 0.0942 H₂O. C = 77.48; H = 5.04. 0.2060 ,, 20.5 c.c. moist nitrogen at 19° and 758 mm. N = 11.40. $C_{16}H_{12}N_2O$ requires C = 77.41; H = 4.83; N = 11.29 per cent.

The constitution of the compound may, à priori, be represented by one of the formulæ,

$$\begin{array}{c} C_{\delta}H_{\delta}\cdot C;C\cdot CO \\ HN;C(C_{\delta}H_{\delta}) > NH; & C_{\delta}H_{\delta}\cdot C;CH\cdot CO \\ I. & II. & III. \end{array}$$

According to the symbol I, it would be the benzamidide of phenylpropiolic acid, and therefore ought to have properties similar to those of benzoylbenzamidine, which, as shown by Pinner ("Die Imidoaether und ihre Derivate," 1892, p. 165), is very unstable, and, under the influence of alkalis or acids, is readily transformed into dibenzamide with evolution of ammonia. But the compound under consideration is remarkably stable; it dissolves freely in alcoholic potash, producing a yellowish solution with a green fluorescence; in aqueous potash, however, it is less soluble. On heating the alkaline solution, benzaldehyde is formed, and after prolonged boiling, ammonia is evolved, but even after 6 hours the greater part of the substance remains unchanged. On adding concentrated hydrochloric acid, the compound at first dissolves, but a solid soon separates from the solution, consisting, no doubt, of the hydrochloride. This is unstable, being decomposed by water into the acid and the original substance. action of boiling hydrochloric acid is similar to that of caustic potash, yielding benzaldehyde and ammonia, but, in this case also the greater part of the compound is not altered. Even when it is heated with concentrated hydrochloric acid at 150-160° for 2-3 hours in a closed tube, only partial decomposition takes place; the solid which remains in the tube, on recrystallisation, melts at 274°, and, on

analysis, gives results similar to those obtained before treatment with the acid.

0.2089 gave 0.5928 CO₂ and 0.0925 H₂O. C=77.39; H=4.97.

The second formula (II) also is excluded, since the substance differs in every respect from diphenylpyrimidone, which is colourless, dissolves readily in alkalis and acids, and melts at 284° (Pinner, *loc. cit.*, p. 254).

It follows therefore that the constitution of the compound has to be expressed by the third formula (III),

which represents it as benzalphenylglyoxalidone, and brings it into close relationship with the glyoxalidines. This conclusion is in harmony with the properties of the compound. It is characterised as a benzal derivative by the colour, and the fact that benzaldehyde is produced by heating it with alkalis or acids. As yet, we have not succeeded in isolating phenylglyoxalidone itself, as the removal of the benzal group takes place slowly, and seems to be accompanied by a destruction of the ring. Further experiments with the object of effecting such a transformation are in progress.

III. Action of Bromins on Ethylic Phenylpropiolate.

Roser and Haselhoff (loc. cit.) obtained, by the action of bromine on phenylpropiolic acid, two stereoisomeric dibromocinnamic acids; the corresponding salts were not isolated owing to the ease with which they decompose. We have repeated their experiments, using ethylic phenylpropiolate instead of the acid, in order to study the behaviour of the additive product towards ethylic sodiomalonate.

Ethylic dibromocinnamate, C_6H_5 CBr. CBr. COOC₂H₅, is formed by gradually adding bromine to a solution of ethylic phenylpropiolate in carbon tetrachloride. In direct sunlight, the union takes place with the greatest ease, and is accompanied by evolution of heat. The compound is a yellowish oil which boils at $174-174.5^{\circ}$ under 10 mm. pressure, and has a sp. gr. 1.6209 at $17^{\circ}/17^{\circ}$. A bromine determination gave the following result:

0.3015 gave 0.3373 AgBr. Br =
$$47.60$$
.
C₁₁H₁₀Br₂O₂ requires Br = 47.90 per cent.

This additive product seems to be a chemical individual, notwithstanding the fact that it yields, on hydrolysis, the two stereoisomeric acids just mentioned, and it is worthy of note that similar cases have

been met with by Fittig and his pupils in the course of their researches on the transformation of isomeric unsaturated acids (Annalen. 1899, 304, 117). Ethylic dibromocinnamate is readily hydrolysed by aqueous caustic potash; even on boiling with concentrated solutions of the alkali for 2 hours, the acid produced suffers only a slight decomposition which is indicated by the brown colour and disagreeable odour of the solution. On adding dilute sulphuric acid to the alkaline liquid, the mixture of the two dibromo-acids is precipitated as an oil which boils at 204° under 15 mm. pressure, and, when cooled, solidifies to a mass of crystals melting at 87°. We experienced the same difficulty in separating the acids as did Roser and Haselhoff, but by repeated crystallisation from light petroleum (b. p. 70-80°) and mechanical separation of the crystals, we succeeded in obtaining the two acids in a pure state. The a-dibromo-acid, which crystallises in colourless plates, when freed from its isomeride, is only sparingly soluble in light petroleum, whilst the β -dibromo-acid forms yellow needles which readily dissolve in the boiling solvent. Our specimen of the a-dibromo-acid melts at 136-137°, instead of at 139°, the melting point given by Roser and Haselhoff. On analysis, the following numbers were obtained:

0.2610 a-acid (m. p. 136°) gave 0.3198 AgBr. Br = 52.15. 0.2973 β -acid (m. p. 100°) , 0.3656 AgBr. Br = 52.32. C₆H₅·CBr:CBr·COOH requires Br = 52.28 per cent.

As already mentioned, ethylic dibromocinnamate does not react with ethylic sodiomalonate, either on digesting the mixture in the presence of alcohol for a day on the water-bath, or on heating it for several hours at 110°.

IV. Action of Ethylic Sodiomalonate on Ethylic Dibromomaleate.

In the investigation referred to in the introduction to this paper, Pum used the product of the interaction of sodium ethoxide and ethylic dibromosuccinate, which he regarded as pure ethylic acetylene-dicarboxylate. This was contradicted by Michael and Maisch (J. pr. Chem., 1892, [ii], 46, 25), who, on repeating his experiments, came to the conclusion that, in this reaction, ethylic acetylenedicarboxylate was not formed, but a substance which, from the results of their analyses, they concluded to be ethylic diethoxysuccinate. Michael and Bucher (Ber., 1896, 29, 1792; see also 1895, 28, 2512), however, have since then found it to be a mixture of the ethylic salts of ethoxyfumaric and unsymmetrical diethoxysuccinic acids. A re-examination of the behaviour of sodium ethoxide towards ethylic dibromosuccinate compelled Pum (Monatsh., 1893, 14, 491) to change his view, and to

admit that the product he obtained was impure, being a mixture of ethylic ethoxysuccinate and acetylenedicarboxylate. Even although this mixture did not possess the characteristic pungent odour of ethylic acetylenedicarboxylate, the presence of this salt in the product of the reaction was, he considered, sufficiently established by the fact that the latter, on hydrolysis, gave acetylenedicarboxylic acid.

In view of these contradictory statements, we have thought it advisable to test Pum's results by starting from pure ethylic acetylene-dicarboxylate. This was obtained, according to Michael's directions (J. pr. Chem., 1892, [ii], 46, 16), from the corresponding acid which we prepared by von Baeyer's method (Ber., 1885, 18, 677). The union of this ethereal salt with bromine takes place with the greatest ease on adding to its solution in carbon tetrachloride the calculated amount (1 mol.) of bromine. The additive product is identical with ethylic dibromomaleate, COOC₂H₅·CBr·COOC₂H₅; it boils at 155—157° under 11 mm. pressure, as compared with 162—164° under 20 mm. pressure observed by Michael (loc. cit., 21) and has a sp. gr. 1·6978 at 25°/25°. Its composition was verified by the following bromine determination:

0.3398 gave 0.3865 AgBr. Br = 48.41. C₈H₁₀O₄Br₂ requires Br = 48.48 per cent.

Ethylic dibromomaleate is readily hydrolysed, the oil disappearing after a few minutes boiling with strong caustic potash. The alkaline liquid, when acidified with dilute sulphuric acid and extracted with ether, yields an oil which sets to a solid mass when left in a vacuum, and consists of dibromomaleic acid mixed with a small quantity of dibromofumaric acid. These acids were separated by Michael's method (loc. cit.), based on the difference in the solubility of their lead salts, and the dibromomaleic acid was identified by the melting point of its anhydride (114°), and by the analysis of its silver salt. Owing to the explosive character of the latter, we determined the amount of silver chloride obtained by adding hydrochloric acid to its solution in nitric acid.

0.2395 gave 0.1400 AgCl. Ag = 44.00. $C_4Br_2O_4Ag_2$ requires Ag = 44.26 per cent.

Ethylic dibromomaleate, as already mentioned, readily reacts with ethylic sodiomalonate, and thus differs most markedly from ethylic dibromocinnamate. The mixture of the former salt (1 mol.) with ethylic malonate ($2\frac{1}{2}$ mols.) and sodium ethoxide ($2\frac{1}{2}$ mols.) dissolved in absolute alcohol, when heated on the water-bath, turns yellow, and finally brown; after 3 hours, the alcohol is evaporated off, the residue treated with water and dilute sulphuric acid, and the oil, which is

precipitated, fractionally distilled under diminished pressure (about 19 mm.). A small quantity boils below 190°; it contains bromine, and is most probably a mixture of ethylic malonate and ethylic dibromomaleate. A considerable amount distils between 190° and 230°, and at 230—250° a thick oil passes over, whilst at the same time decomposition occurs.

The fraction which boils between 190° and 230° partially solidifies to a crystalline mass, which is freed from adhering oil by the aid of a pump, and recrystallised from alcohol. In this way, long, colourless needles are obtained which melt at 76°. The identity of this compound with ethylic ethanetetracarboxylate, (COOC₂H₅)₂CH·CH(COOC₂H₅)₂, has been ascertained by comparison with a specimen prepared by Bischoff's method, and also by the following analyses:

The properties of this compound agree with those of the substance which Pum obtained, and which he regarded as ethylic dimalonylmaleate.

The fraction of high boiling point produced in the above reaction undoubtedly contains ethylic propenetetracarboxylate, which owes its formation to the union of the ethylic salts of malonic and acetylene-dicarboxylic acids. Our attempts to obtain this compound in a pure state by redistillation in a vacuum have been unsuccessful, owing to partial decomposition, a fact also observed by Michael (*J. pr. Chem.*, 1894, [ii], 49, 20), yet the analyses of the fractions boiling at (I) 240—243° and (II) 249—250°, respectively, under 19 mm. pressure, give results sufficiently close to those required by the formula COOC₂H₅·CH:C(COOC₂H₅)·CH(COOC₂H₅)₂.

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I. 0.2268 gave 0.4475 CO_2 and 0.1385 H_2O. C=53.81; H=6.78. II. 0.2320 ,, 0.4595 CO_2 ,, 0.1390 H_2O. C=54.01; H=6.65. C_{15}H_{22}O_8 requires C=54.54; H=6.67 per cent.
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In conclusion, we express our thanks to the Government Grant Committee of the Royal Society for assistance in carrying out this investigation.

GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.



XCIII.—A Contribution to the Chemistry of the Mandelic Acids.

By ALEX. McKenzie, M.A., D.Sc.

THE following work was undertaken in order to obtain d- and l-mandelic acids for the preparation of the optically active phenylalkyloxyacetic acids recently described (Trans., 1899, 75, 753). Although recourse was eventually had to amygdalin as a convenient source of l-mandelic acid, the results obtained in a series of experiments on the resolution of the inactive acid into its optical isomerides are put on record, in view of the attention at present being given to the general subject.*

Mandelic acid had previously been resolved into its active components by Lewkowitsch (Ber., 1883, 16, 1569), who isolated the d-acid, first by employing Penicillium glaucum, and later by means of a nucleus of cinchonine d-mandelate; for the preparation of the l-acid, he used Saccharomyces ellipsoideus. As I had not cinchonine d-mandelate at my disposal, the inactive acid was accordingly resolved by alkaloids.

Preliminary experiments with cinchonine, cinchonidine, brucine, and morphine, in aqueous solutions, and with cinchonidine, in alcoholic and benzene solutions, showed that the difference in solubility between the alkaloidal d- and l-salts was not such as to afford a convenient method. The partial resolution with cinchonidine may be quoted, as it possibly illustrates Ladenburg's views regarding the resolution of an acid by alkaloids.

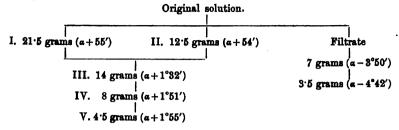
Partial Resolution by Cinchonidine.

20 grams of mandelic acid were dissolved in 1200 c.c. of water, and the boiling solution neutralised with the calculated quantity of alkaloid. The crystalline salt (I), which separated on cooling, was collected, and from the filtrate, after a day's interval, a further crop (II) was removed. As the two crops were equally active, they were united and recrystallised several times, the progress of the separation being noted as follows.

One gram of the air-dried salt was dissolved in the requisite amount of water; the cinchonidine which was precipitated by a definite volume of standard ammonia solution was collected and washed with water, the washings being added to the solution of the ammonium salt; the latter was next evaporated to less than the volume required to fill a 4 dcm. tube, and when just ammoniacal was made up to the volume necessary to fill the tube. The separation is represented by the fol-

^{*} Rimbach's paper, "Ueber Spaltung und Eigenschaften der Mandelsäure" (Ber. 1899, 32, 2385) appeared after this work had been sent in for publication.

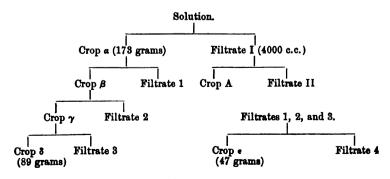
lowing scheme, the rotations being those observed for the ammonium salt:



The acid obtained from V by precipitation of the alkaloid with ammonia, acidification of the ammonium salt, and extraction with ether, melted at 113—117°, and had the specific rotation +49°, whilst the pure d-acid, described by Lewkowitsch (loc. cit.), had for similar concentration the value +156°. The positive rotations of the ammonium salts were probably lowered slightly by the presence of a little levorotatory cinchonidine dissolved in the process of washing, but the values are comparable, as like conditions were observed in each determination. The rotations of the ammonium salt in IV and V are practically identical, and yet the acid from V had not nearly reached the full activity. It is therefore quite possible that in this case a partially racemic alkaloidal salt had been formed.

Resolution by Quinidins.

100 grams of mandelic acid were dissolved in 4850 c.c. of water, and the hot solution neutralised by the calculated quantity of quinidine. On cooling, the mixture of the alkaloidal salts tended to separate as an oil, but crystallisation soon started in the form o needles. The following scheme indicates the method of separation:



Crop δ , after removal of the alkaloid with ammonia, yielded 21 grams of an almost pure, active mandelic acid (m. p. 127—131°), from which,

after two crystallisations from water, the pure l-acid was obtained, melting at 132°, and with the specific rotation -156.3° for c = 3.093.

Lewkowitsch gives the melting point as 132.8° , and the specific rotation for similar concentration as -156.4° . The acid obtained from crop ϵ , after one recrystallisation from water, melted at $122-126^{\circ}$, and, together with the levorotatory aqueous mother liquors from the crystallisation of the pure acid, was worked up subsequently.

The acid obtained from filtrate II was twice crystallised from water and yielded the d-acid, melting at $132-133^{\circ}$ and with the specific rotation $+158\cdot2^{\circ}$ for $c=3\cdot5187$.

Preparation of the Active Acids by means of Cinchonine.

By the addition of a nucleus of cinchonine d-mandelate to an aqueous solution of mandelic acid which had been previously neutralised by cinchonine, Lewkowitsch obtained at once a crop of pure cinchonine d-mandelate, and from this the pure d-acid. On repetition of his method under varying conditions, an oil usually separated on cooling the solution, and I invariably obtained a mixture of the alkaloidal salts (or, possibly, a partially racemic salt). The cinchonine d-salt, used as a nucleus, was crystalline, and was prepared from the d-acid, obtained by the quinidine resolution just described. One experiment, in which the nucleus was added to the hot solution before the separation of oil and remained undissolved, yielded a salt which gave an acid melting at 115—125°, and containing, according to Lewkowitsch, approximately 40 per cent. of the active form. The success of this resolution doubtless depends very materially on the temperature at which crystallisation of the d-salt is induced.

For the preparation of the active mandelic acids on a larger scale, 200 grams of inactive acid were dissolved in about 13 litres of boiling water and neutralised with the calculated quantity of cinchonine. Before any turbidity was evident, crystallisation was induced in the warm solution by a nucleus of cinchonine d-mandelate. The salt which separated yielded about 90 grams of active acid, which was recrystallised from water until the melting point was sharp. The pure acid thus obtained had the following rotation:

$$l = 2.2$$
, $c = 3.9525$, $a_D^6 = +13.80^\circ$, $[a]_D = +158.7^\circ$.

The filtrate from which the cinchonine salt had been separated measured about $8\frac{1}{2}$ litres. The *l*-acid, obtained from this, was repeatedly crystallised from water until it melted sharply; it then had the following rotation:

$$l=1$$
, $c=3.8295$, $a_D^7=-6.12^\circ$, $[a]_D=-159.8^\circ$.

To obtain a further quantity of d-acid, the mother liquors of the

dextro-acid were again neutralised with cinchonine, and the treatment repeated as previously described. The mother liquors of the lævo-acid were also neutralised with quinidine, and by help of a nucleus of quinidine *l*-mandelate yielded a further quantity of *l*-acid.

The difference in solubility between the inactive and active acids in water, the inactive at the ordinary temperature being about twice as soluble as the active, was utilised for the isolation of the active acids in the preceding experiments. On repeated evaporation of aqueous solutions, however, it was found that the separation of the solid acid became more difficult from the formation of a slight amount of a smeary product, possibly an anhydride. The acids also are partially decomposed at 100°: for instance, 0.6518 gram of the inactive acid lost 0.1083 gram when heated for 41 hours at 100°, and 0.6082 gram of the d-acid, under similar conditions, lost 0.0830 gram. Benzaldehyde is slowly evolved, and the white acids become vitreous and yellowish with the formation of diphenylmaleic anhydride.

From the pure active acids, the salts of various alkaloids were prepared by neutralisation with the calculated amount of alkaloid. In each case, a crop was withdrawn from the solution and air-dried on clay. The solubilities in water at 18—20° were determined by Victor Meyer's method, S representing the number of parts dissolved by 100 parts of water.

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Cinchonine.	d-Salt. Prisms grouped in rosettes, m. p. 79—80°. $8=1.29$	l-Sall. Appearance similar to d -salt, m. p. 165° with decomposition. $8=2.47$
Cinchonidine.	Needles in rosettes, m. p. 185—186° with decomposition. S=0.89 S (in alcohol)=5.4 (t=19°)	Long, prismatic needles, m. p. $189-190^{\circ}$ with decomposition. $S=1^{\circ}22$ S (in alcohol)=8.6 $(t=19^{\circ})$
Brucine.	Rosettes of prisms with pointed ends. m. p. 135—136°. S=9.43	Slender, silky needles, m. p. 97—98°. S=10·48
Strychnine.	Soft, feathery crystals, m. p. $115-116^{\circ}$. S=2.41	Hard, gritty cubes, m. p. 184—185°. S=5.40
Quinidine.	Long, silky needles, m. p. 110°. S=1·15	Rhombic prisms, m. p. 100—101°. S=0.49
Quinine.	Needles, begins to decompose at 180°. $8=1.8$ S (in alcohol)=8.3 ($t=20^{\circ}$).	Needles, begins to decompose at 202°. S=0.46 S (in alcohol) = 1.8 ($t=20^{\circ}$).

The quinine salts are slightly acid to litmus, and it appears that their solutions cannot be evaporated without hydrolysis taking place, so that what eventually separates from the solution is a mixture of the salt with quinine. Similar hydrolytic dissociation has been observed by Marckwald and his pupils (*Ber.*, 1896, 29, 53; 1898, 31, 786).

Resolution by Quinine and Morphine.

It appeared from the preceding observations that mandelic acid could be conveniently resolved by quinine in alcoholic solution. By the addition of a nucleus of quinine *l*-mandelate to an alcoholic solution of the acid in which the calculated amount of quinine had been dissolved, the pure quinine *l*-salt crystallised out, and from this the pure *l*-acid was obtained.

The morphine salts were both readily soluble in water, and did not crystallise in a vacuum. They differ remarkably from one another in their solubility in alcohol; the d-salt dissolves easily, but the l-salt only sparingly, and crystallises from its alcoholic solution in long, rhombic prisms. This difference affords a ready method for procuring l-mandelic acid; the aqueous solution of the inactive acid, after neutralisation with morphine, is concentrated to a gum, and from this the morphine l-salt is precipitated by the addition of an excess of absolute alcohol.

Attempts to Resolve Mandelic Acid by Crystallisation of its Enantiomorphous Forms.

Although spontaneous crystallisation has been successfully applied only in a few rare cases for the resolution of inactive compounds into optically active isomerides, the following experiments were undertaken in the hope that the active mandelic acids might be obtained by this method. By the addition of an active nucleus to a solution supersaturated with respect to the corresponding inactive substance, it appeared possible on theoretical grounds that conditions might obtain in which crystallisation of the single enantiomorph would be induced, as in the case of Purdie's resolution of lactic acid by the zinc ammonium salt. Besides, mandelic acid from the high degree of activity of its active forms seemed peculiarly well adapted for the purpose in question, because, even if the resolution took place in the slightest degree, it would be so much more readily recognised than in the case of feebly-rotating substances. Accordingly, a number of metallic salts of the mandelic acids were prepared with the view of ascertaining whether any would lend themselves to separation by crystallisation. The salts were prepared from the pure acids by neutralisation with the corresponding metallic carbonate, analysed, and their solubilities in water determined.

Calcium.	Inactive. Plates. Anhydrous. $S=1.7 (t=24^{\circ})$	Active. Oblong, pearly plates. Anhydrous. $S = 2 \cdot 1 \ (t = 24^{\circ})$
Strontium.	Anhydrous. $S=4.3$ ($t=15^{\circ}$)	Plates. Anhydrous. $S=8.8 (t=15^{\circ})$
Barium.	Large, glassy plates and prisms in resettes. Contains $\frac{1}{2}H_2O$. S=8·3 $(t=19^\circ)$	Rhombic prisms. Contains $\frac{1}{2}H_2O$ $S=6.9$ ($t=19^\circ$)
Magnesium.	Needles. Anhydrous. $S=1.8 (t=16^{\circ})$	Anhydrous. S=4.5 (t=16°)
Zinc.	Hexagonal plates. Anhydrous. $8=0.29 (t=19^{\circ})$	Needles. Anhydrous. $S=0.26 (t=19^{\circ})$
Cadmium.	Anhydrous. $S=0.1 (t=16^{\circ})$	Anhydrous. $8=0.2 (t=16^{\circ})$

The following attempts were made to resolve mandelic acid by crystallisation of the enantiomorphous forms.

- (1) Crystallisation from acetic acid. A solution of mandelic acid in glacial acetic acid, with which it readily forms supersaturated solutions, was made of such a degree of concentration that a nucleus of active acid induced crystallisation, although none had occurred during a period of 12 hours prior to its introduction. The acid brought down by the nucleus proved to be inactive. In the course of several experiments, the labile form of mandelic acid previously noted by W. W. J. Nicol (*Proc. R.S. Edin.*, 1897, 21, 478) was observed.
- (2) Experiments with aniline mandelate and paratoluidine mandelate, which readily form supersaturated solutions in aqueous alcohol, yielded similar results.
- (3) Negative results were also obtained with inactive barium hydrogen mandelate containing 1H₂O, which forms supersaturated solutions in water.
- (4) Attempts to isolate double salts were unsuccessful. One instance may be quoted as showing the mode in which resolution was attempted. Barium d-mandelate was heated on the water-bath with excess of ammonium d-mandelate and from the syrupy solution, after filtration, crystals separated which were used as nuclei. Inactive barium mandelate was heated with ammonium mandelate and from the solution, after the addition of a nucleus to induce crystallisation, an inactive crop of crystals separated.

Zinc mandelate is very slightly soluble in ammonium mandelate, but in presence of alcohol and excess of ammonia it dissolves readily in an aqueous solution of the salt, and, on cooling, a well crystallised salt separates in needles quite different in appearance from zinc mandelate. After washing with alcohol and drying in air, it lost

12.40 per cent. of water at 110° (calculated for $C_{16}H_{14}O_{e}Zn\cdot NH_{3}+3H_{2}O$; $H_{2}O=12.32$ per cent.). The anhydrous salt yielded 17.09 per cent. of zinc, calculated 17.01. The salt appears to be analogous to the compounds of ammonia with zinc lactate described by Lutschak (*Ber.*, 1872, 5, 30), and by Purdie (Trans., 1893, 63, 1156). On the addition of an active nucleus, prepared similarly, to the solution of zinc mandelate in aqueous ammonium mandelate in presence of alcohol and excess of ammonia, the crop of crystals induced by the nucleus was invariably found to be inactive.

Conclusions.

With regard to the relative solubilities of the alkaloidal salts examined, the following table indicates the manner in which the resolution of the acid would be effected with each particular alkaloid, the sign of rotation of the alkaloid being indicated under I, and that of the acid forming the less soluble alkaloidal salt under II.

I.		II.	I.	II.
d	Cinchonine	\boldsymbol{d}	l Strychnine	ď
Z	Cinchonidine	d	l Brucine	d
Į	Quinine	Z	l Morphine	l
d	Quinidine	Z	-	

The d- and l-salts of the same alkaloid are in several cases superficially alike when viewed under the microscope, but whether the salts are really isomorphous could only, of course, be shown by crystallographic measurements. The only case recorded where the alkaloidal salts of d- and l-acids are crystallographically the same is that of the brucine salts of the active valeric acids (Schütz and Marckwald, Ber., 1896, 29,55). The speedy resolution of a resolvable acid by an alkaloid is no doubt dependent, not solely upon the difference of solubility between the two alkaloidal salts at any fixed temperature, but also upon their similarity or dissimilarity in crystalline structure. That cinchonidine, for instance, acts so imperfectly in resolving mandelic acid may perhaps be ascribed partly to the isomorphism of its salts.

The salt of the d-acid with cinchonine and cinchonidine, and of the l-acid with quinine and quinidine, are the more insoluble. These results are, so far, in accordance with Winther's theory as to the resolution of a racemic compound by alkaloids (Ber., 1895, 28, 3000); the theory, however, is not tenable when the other alkaloids are considered, as strychnine and brucine should act like quinine and quinidine, and morphine like cinchonine and cinchonidine.

No great differences in solubility between the inactive and active metallic salts were observed, such as, for example, Frankland and Appleyard found with the metallic glycerates. The crystalline forms of the active salts were, of course, superficially alike in all cases, and evidently different from the corresponding inactive forms—a sure criterion that the inactive salts are racemic and not pseudoracemic, or The solubility of the active salt is generally greater than that of the inactive, which is a further indication that the inactive salt is racemic. In the case of the barium salt only is the solubility of the active form less, hence the possibility of the inactive barium salt being a dl-mixture. The following experiment, however, proves that such is not the case, and that the inactive barium salt is, like the others, racemic. A mixture of 0.1 gram of L-mandelic acid and 1.9 grams of inactive mandelic acid was converted into barium salt, from the solution of which 1.25 grams of inactive salt were withdrawn, the filtrate, on the other hand, rotating $a_0 = -1.6^{\circ}$ in a 2 dcm. tube.

Inactive mandelic acid is itself a racemic compound, as, according to Walden, it crystallises in the rhombic form, the active acids being monochinic. As a general rule, the r-compound melts at a higher temperature than the active; the converse, however, is the case with mandelic acid, the inactive acid melting at 119°, the active at 133°. The melting point of the active acid is, however, always lowered by admixture with the inactive compound, and, in accordance with Bakhuis Roozeboom's views (Zeit. physikal. Chem., 1899, 28, 506), this indicates also that inactive mandelic acid is a racemic compound.

Whilst cases of the separation of one enantiomorph by spontaneous crystallisation with the aid of double salts are known, there are, as yet, no examples of this, using the simple metallic salts. The mandelates are nearly all anhydrous, and not prone to form double salts. With the lactates and tartrates it is different, and the ease with which zinc lactate, for instance, dissolves in ammonium lactate to form the double salt may be attributed partly to the fact that zinc lactate contains water of crystallisation.

Two reasons may be assigned for the negative results on the resolution of mandelic acid by crystallisation.

- (1) The "transition temperature" had not been reached. Many of the experiments were conducted at temperatures varying from 0° to 20°, but very few at temperatures above that of the atmosphere. Now Kenrick (*Ber.*, 1897, 30, 1749), for instance, has shown that r-ammonium hydrogen malate is not converted into the dl-mixture till the high "transition temperature" of 73° is reached.
- (2) Hemihedrism is either absent or masked in the crystals of the active isomerides.

Pasteur's statement, that all substances optically active in solution crystallise in hemihedral forms, has been discussed, amongst others, by Walden and Hermann Traube (Ber., 1896, 29, 1692, 2446, &c.). The determination of hemihedrism is frequently attended with difficulty; simple goniometric measurement is often inadequate, and many cases are known where earlier investigators failed to detect hemihedrism, the existence of which was later established in the particular crystals by pyroelectrical and other special methods. The rotation of a substance in solution must be ascribed to molecular, and not to crystallographic, structure, and the greater the rotation the greater the molecular asymmetry. If, then, crystallographic asymmetry is, as Pasteur supposed, concomitant with rotation in solution, those substances which in solution exhibit marked optical activity ought to exhibit distinct hemihedrism: yet, as Walden points out, highly active bodies, like certain derivatives of santonine, terpenes, &c., do not exhibit hemihedrism at all. Traube, however, maintains that in all cases where the search for hemihedrism has been accurately conducted, Pasteur's statement is confirmed.

Purdie has shown, with zinc ammonium lactate, that the r-form is stable at low, and the dl-mixture at higher temperatures. The separation of the one enantiomorph, at a temperature at which the r-form is stable, was possible, because the solution at the lower temperature remained supersaturated towards, not only the dl-mixture, but also towards either active form separately. The active zinc ammonium lactates have not been examined crystallographically, but hemihedrism would doubtless be well defined from the crystal measurements alone. In the experiments made with mandelic acid, on the other hand, it is quite likely that in the active acids and active salts used no hemihedrism would be observed, or, at least, if it did exist, it would be masked, and could be detected only by special methods.

It seems to me that a necessary condition for the separation of one active isomeride by crystallisation, such as that attempted with mandelic acid, is that the hemihedrism of the nucleus added shall be so pronounced as to be evident from crystal measurement. If hemihedrism is absent or masked, the addition of an active nucleus to a supersaturated solution of an inactive substance can induce separation of inactive substance only, and, in this case, the "transition temperature" has no bearing on the problem.

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XCIV.—Non-existence of the so-called Suboxide of Phosphorus.

By DAVID LEONARD CHAPMAN and F. AUSTIN LIDBURY.

THE purpose of the present paper is to show: firstly, that the grounds adduced by previous investigators for the existence of a definite sub-oxide of phosphorus having a formula P₄O are insufficient; secondly, that the so-called suboxide, prepared by their methods, has properties identical with those of red phosphorus; thirdly, that, when the substance is carefully purified and analysed, the percentage of phosphorus is invariably higher than that required by the formula.

Le Verrier (Annalen, 1838, 27, 167) examined the red substance obtained by allowing pieces of white phosphorus, covered with phosphorus trichloride, to remain in air, and found that the percentage of phosphorus agreed closely with that required by the formula P₄O. Von Schrötter some time afterwards (Wien. Sitz.-Ber., 1852, 8, 256) cast doubt on the existence of a suboxide, believing the substance to be merely an impure form of amorphous phosphorus which had been discovered by him in 1845.

Goldschmidt and Reinitzer (Ber., 1880, 13, 845) prepared and examined a red substance which closely resembled the "suboxide" described by Le Verrier, and their experiments are generally accepted as affording conclusive proof of the existence of a substance of definite composition P.O. This being so, we will describe briefly their experiments and conclusions. They obtained the substance by the action of phosphorus oxychloride either on zinc, magnesium, or aluminium at 100°, or on white phosphorus at 250°. Of the product prepared from white phosphorus, they say (loc. cit., p. 850), "This substance has the composition of P₄O, but not its properties; it is not attacked by water and alkalis; moreover, it does not reduce the noble metals from their salts, and it approximates in its behaviour to amorphous phosphorus." They do not seem to have been aware that the substances prepared from the oxychloride also have properties identical with those of amorphous phosphorus, as will be seen later. Analyses of the dried substance obtained by the action of zinc on phosphorus oxychloride gave only 82.4-87.4 per cent. of phosphorus, whereas the formula P₄O requires 88.57 per cent. This deficiency of phosphorus was attributed to the presence of water. In one case, a carefully prepared specimen was divided into two portions; the phosphorus was estimated in one as pyrophosphate, and the carbon and hydrogen in the other by combustion with K₂Cr₂O₇. The assumption was made that the hydrogen was present as water, the amount of which, together

with that of the carbon (0.102 per cent.), was subtracted from the weight of the sample taken, and the atomic ratio of phosphorus to oxygen in the remainder was then found to be 4.01:1.

Michaelis and Pitsch (Ber., 1899, 32, 337) have recently prepared a yellow substance which they believe to be the suboxide. It was obtained by precipitating with dilute hydrochloric acid the red solution which results from the action of an alcoholic aqueous solution of caustic alkalis on white phosphorus. They, however, observe that some samples contained more than the 88.57 per cent, of phosphorus required by theory, a fact which they suggest is due to the precipitation of phosphorus in cases where the solution of hydrochloric acid was not sufficiently dilute. We have repeated their experiments. using very dilute acid, and find that, if the precipitate is merely dried with care, it contains 90.5 per cent. of phosphorus. If the suggestion of Michaelis and Pitsch be admitted, 19 per cent. of the precipitate should consist of uncombined phosphorus. It seems more probable that their product is merely an impure form of red phosphorus. especially as its appearance and properties prove to be identical with those of red phosphorus, when prepared by methods which give separated particles (compare Pedler, Trans., 1890, 57, 599).

Experimental.

In preparing the "suboxide" for the purpose of comparing its properties with those of red phosphorus, we followed closely the directions given in the papers of Goldschmidt and Reinitzer, and of Michaelis and Pitsch. The following is an account of the experiments.

1. White phosphorus was obtained in a state of purity and fine subdivision by melting under a solution of chromic acid and violently agitating during solidification. A solution of aqueous alcoholic potash containing 2 vols. of alcohol and 1 vol. of a 10 per cent. aqueous solution of caustic potash was allowed to act on the phosphorus. It was noticed that a stronger solution was obtained by occasional than by continued agitation; apparently the reaction is facilitated by a slight amount of local heating, which continual agitation prevents. The dark red liquid thus obtained was filtered and allowed to run drop by drop through a second filter into a very dilute solution of hydrochloric acid which was kept constantly in motion by an automatic stirring apparatus. After the yellow, flocculent precipitate had subsided, it was washed by decantation several times with hot water, collected on a filter, and washed successively with hot water, boiling alcohol, and ether. It was then transferred to a porous plate and dried in a

vacuum. Lastly, it was ground up and left in a vacuum over phosphorus pentoxide for several days.

- 2. Phosphorus oxychloride was heated with pure zinc foil in a Geissler flask for 6 hours on a water-bath, and the product then poured gradually into a large beaker of water. The hydrochloric acid so formed was sufficient to dissolve the remaining zinc. The precipitate was allowed to settle, collected on a filter, boiled with concentrated hydrochloric acid to remove any traces of zinc, washed, and dried in the same manner as the specimen just described. A similar preparation was made, with the substitution of magnesium for zinc.
- 3. Red phosphorus was prepared in a state of fine subdivision by Pedler's method (loc. cit.). A strong solution of phosphorus in carbon bisulphide was sealed up in a glass tube in such a manner as to leave only a bubble of enclosed air. The tube was exposed to strong sunlight for several days during July. The yellow, flocculent precipitate which soon began to form had the exact appearance of the precipitate obtained when the red liquid resulting from the action of aqueous alcoholic potash on white phosphorus is acidified as described above. When sufficient red phosphorus had thus been formed, the contents of the tube were poured out, and the precipitate washed several times with carbon bisulphide. The two "suboxide" specimens and the red phosphorus obtained by the last method were examined in order to determine whether any difference in physical or chemical properties could be detected.

The colour both of the "suboxide" and of the red phosphorus may vary from yellow to orange-red, according to the state of aggregation. When the particles are well separated, as after long desiccation over phosphorus pentoxide in a vacuum, the colour is light yellow, but when they are more closely collected together, as after imperfect drying or when mixed with glycerine, the colour approximates to red. The respective tints are the same in each case, proving that the same kinds of light are absorbed in the same proportion by each specimen.

When examined under a microscope (one-sixth inch objective) all the specimens are seen to consist of extremely small, translucent particles transmitting yellow light, as is the case with all varieties of red phosphorus.

In order to compare the temperature of sublimation of the alleged suboxide with that of red phosphorus, a specimen of each was placed in a tube connected by a capillary with a Sprengel pump. During exhaustion, a gas smelling of phosphine was evolved from the "suboxide" specimens. The pump was kept in action, and when a vacuum was obtained the temperature of the tube was gradually raised by

introducing it into an air-bath, with the result that further quantities of gas were evolved, and also moisture, which condensed in the cool capillary tube. From the red phosphorus prepared by Pedler's method, only very small quantities of gas, destitute of the smell of phosphine, were evolved, and no moisture was noticed. On raising the temperature above 100°, it was at first thought that a difference had been detected in the specimen prepared by the action of zinc on phosphorus oxychloride, since a small quantity of phosphorus volatilised at 130°. This was traced, however, to the presence of white phosphorus which is formed during the action of water on the mixture of zinc, phosphorus oxychloride, and the products of their reaction. Still larger quantities are formed when magnesium is used. After removal of the phosphorus by carbon bisulphide, the specimen behaved in the same way as the others, and all began to give off vapour of phosphorus at about 350°.

Both red phosphorus and the "suboxide" are acted on rapidly by caustic alkalis with formation of phosphine. The action of potassium hydrate does not, therefore, constitute a difference, as was thought before Pedler showed that red phosphorus in a finely divided state does not resist the action of that agent. The reason of the comparatively slow action of caustic alkalis on the commercial variety of red phosphorus is to be found in the fact that the particles are closely cemented together in large blocks which expose but a small surface to the action of reagents (this vol., p. 737). This is probably why the specimen obtained by Goldschmidt and Reinitzer at a comparatively high temperature (250°) by the action of white phosphorus on phosphorus oxychloride did not appear to be acted on by caustic alkalis to any appreciable extent.

A fairly strong aqueous alcoholic solution of caustic potash dissolves both red phosphorus and the "suboxide," forming the ruby-red liquid noticed by Michaelis and Pitsch (loc. cit.), and in each case dilute hydrochloric acid reprecipitates red phosphorus in the characteristic flocculent condition already referred to.

All the specimens were attacked slowly by water with evolution of phosphine, and after filtration the filtrates reduced silver nitrate solution. Thus, both red phosphorus and the "suboxide" are simultaneously oxidised and reduced by water, phosphine and either hypophosphorous or phosphorous acid, or a mixture of both, being formed. One or both of these acids must therefore be formed during the preparation of the supposed suboxide, and probably, with water, constitute the chief impurity.

Both the "suboxide" and the red phosphorus, when exposed to moist air, smell of phosphine, and are gradually converted into phosphoric acid.

Analyses.—Specimens were prepared for analysis by the following methods:

I. By the method of Michaelis and Pitsch, already described.

II. By the action of zinc on phosphorus oxychloride, also described above. The small quantity of white phosphorus which the substance contained was expelled by heating it in a vacuum for twelve hours at 150°.

III. By the action of magnesium on phosphorus oxychloride. In this case the white phosphorus was removed by carbon bisulphide, after washing thoroughly in the same manner as specimens I and II. The carbon bisulphide was removed by ether; the powder was left in a vacuum over phosphorus pentoxide for three days, and finally heated for five hours in a vacuum at 150°. No phosphorus vapour was evolved, but even after the long desiccation it had received, small quantities of water and phosphine were given off.

IV. A substance, identical in appearance and properties with the foregoing, was prepared by allowing a solution of hypophosphorous acid to drop slowly into phosphorus trichloride, contained in a Geissler flask and heated on a water-bath. The washing and drying operations were the same as in III.

About 0.2 gram of the specimen was introduced into a Geissler flask and covered with dilute hydrochloric acid, pure concentrated nitric acid was then allowed to slowly flow down the condenser, the flask being shaken from time to time, and when all had dissolved, concentrated nitric acid was added until the flask contained about 100 c.c. of the liquid. It was then heated on a water-bath for twelve hours, concentrated hydrochloric acid being added in small quantities at intervals during the first two hours: When cool, the contents of the flask were washed out into a large porcelain basin, and the excess of acid evaporated off. The residual syrup was then diluted, and the phosphoric acid precipitated, first as phosphomolybdate, then twice as magnesium phosphate, according to the detailed directions given by Fresenius. We obtained the following results:

Specimen I (2 analyses).

- (a) 0.1245 gave 0.4045 Mg₂P₂O₇. P = 90.5 per cent.
- (β) 0.26405 ,, 0.86095 Mg₂P₂O₇. P = 90.8 ,

Specimen II (2 analyses).

- (a) 0.27565 gave 0.9050 $Mg_2P_2O_7$. P = 91.41 per cent.
- $(\beta) 0.2279$, $0.7490 \text{ Mg}_2\text{P}_2\text{O}_7$. P = 91.45

Specimen III

 $0.1369~gave~0.4500~Mg_{2}P_{2}O_{7}.~~P=91.51~per~cent.$

Specimen IV.

0.2019 gave 0.7161 $Mg_2P_2O_7$. P = 94.52 per cent. P_4O requires P = 88.57 per cent.

When specimens II and III were dissolved in aqueous caustic potash, a black residue was left. This was not the case with IV, and may account for the higher percentage of phosphorus which it contained.

Discussion of Results.—If, as these results indicate, the substance which has been described as a definite suboxide is none other than an impure form of red phosphorus, it becomes necessary to form some idea of the nature of the impurity.

Direct evidence has been adduced to show that it is very difficult to completely remove the adhering moisture, as water vapour is evolved when the substance is heated in a vacuum even after prolonged desiccation. Goldschmidt and Reinitzer have also called attention to this fact. As mentioned above, in most cases our specimens were heated in a vacuum at 150° before analysis; water, however, even at ordinary temperatures, acts on red phosphorus, forming phosphine and the lower acids. When the phosphorus is in a fine state of division, and consequently exposes a large surface, considerable quantities of these products may be formed. All the substances which have been mistaken for PAO have been in such a finely divided condition; all of them, moreover, have been exposed to the action of water during their preparation. The phosphine evolved on heating them in a vacuum may either be due to the direct action of adhering water, or to the decomposition of phosphorous or hypophosphorous acid present on the surface of the particles.

We have, therefore, come to the conclusion that the supposed suboxide, P₄O, is identical with red phosphorus, since no chemical or physical property has yet been observed by which they may be distinguished from one another; the impure nature of the red phosphorus described as the suboxide we believe to be due to the hygroscopic nature of the microscopic particles and the tendency they exhibit to undergo surface oxidation in the presence of water. Finally, our analyses are entirely inconsistent with the hypothesis that a definite oxide of the formula P₄O exists.

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XCV.—The Chlorine Derivatives of Pyridine. Part III.

The Interaction of Chlorine and Pyridine Hydrochloride.

By W. J. SELL, M.A., F.I.C., and F. W. Dootson, M.A.

In a former communication (Trans., 1898, 73; 432), the authors described a method of obtaining a considerable number of the chlorinated derivatives of pyridine by the direct action of phosphorus pentachloride on this substance. The experimental difficulties, however, were considerable, and it was of importance that some readier method should, if possible, be found for bringing about the desired substitution, since, in order to study the properties and reactions of the chloropyridines in any degree satisfactorily, considerable quantities of these substances would be required. With this object in view, the authors have studied the direct action of chlorine on pyridine hydrochloride. The action of chlorine on the base itself has already been described (Trans., 1898, 73, 442), and has been shown to be of little utility for the preparation of chloropyridines.

In this series of experiments, pyridine was saturated with hydrogen chloride, the amount of gas absorbed being usually about 50 per cent, in excess of that required for the formation of pyridine hydrochloride. The substance thus obtained fuses at a much lower temperature than the normal compound, and was thus more suitable for the purpose in view. Chlorine was led through this product, a temperature of 115—120° being maintained by means of a thermostat. The materials were all carefully dried, for reasons which will appear later. The operation is a long one, requiring several weeks for completion; but as the yield is comparatively good and large quantities of material can be operated on at one time, the method is regarded as a very satisfactory one for the preparation of such of the chloropyridines as are described below.

In the course of these experiments, the action of various so-called catalytic agents as chlorine carriers was tried, such as sulphur chloride, phosphorus pentachloride, aluminium chloride, and iodine,* but no material advantage resulted from their use.

* In those experiments in which iodine had been used as a chlorine carrier (to the extent of 1 per cent. of the weight of pyridine hydrochloride taken), the clear liquid left in the flask after the steam distillation (p. 982) deposited golden yellow crystals in long, flat plates, sometimes 5 cm. long and 1 cm. broad. This substance melted at 180° (uncorr.) and was identified as the hydrochloride of an additive compound of pyridine, chlorine, and iodine, C_kH_kN,ICl,HCl, described

After the chlorination had proceeded for a few days, the contents of the flask were seen to separate into two layers, the lower of which increased from day to day, and when it was stopped on the disappearance of the upper layer, the flask, on cooling, contained a solid or semi-solid mass of nearly colourless products, carbonaceous matter being entirely absent.

In the first experiments, the chlorination was stopped at an earlier stage, and the upper layer removed for examination. It was found to consist, for the greater part, of unchanged pyridine hydrochloride, but contained a certain amount of chloropyridines, and a substance to be described later. The following compounds were isolated:

- 1. A light, colourless, feathery sublimate, which settled in the neck and colder portions of the flask. This is probably the compound described by Anderson (*Trans. Roy. Soc. Edin.*, 1857) and mentioned by the authors (Trans., 1898, 73, 443).
 - 2. A trichloraminopyridine, m. p. 159-160°.
- 3. A compound, $C_{10}Cl_{11}HN_2$, which, by the action of moisture, is converted into a second compound, $C_{10}Cl_0OHN_0$.
 - 4. A compound, C10Cl2OHNo.
- 5. A dichloropyridine, identical with that described by Königs and Geigy (Ber., 1884, 17, 1833).
 - 6. A tetrachloropyridine, m. p. 21-22°.
 - 7. Pentachloropyridine.

Of the ten theoretically possible isomerides of the formula $C_8NHCl_8\cdot NH_9$, the following have been described:

- 1. A trichloro-a-aminopyridine, in which the position of the chlorine atoms is unknown. This compound was obtained by the action of phosphorus pentachloride on β -oxyglutaramide (Anschütz, Richter's Organische Chemie, 2, 573), and melts at 143—144°.
- 2. A trichloraminopyridine, obtained by the action of phosphorus pentachloride on glutazine by Stokes and Pechmann (*Amer. Chem. J.*, 1886, 6, 377), which melts at 157.5°, and has been shown to have formula I.

3. A trichloraminopyridine, obtained by the authors from tetrachlorisonicotinic acid by the action of ammonia. This compound

by Pictet and Krafft (Bull. Soc. Chim., 1892, [iii], 7, 72). This was confirmed by recrystallising it from dilute alcohol, when colourless crystals were obtained which, like Pictet and Krafft's compound, C₅H₅N,ICl, melted at 132—133°.

melts at $158-160^{\circ}$, and has the remaining hydrogen atom in the γ -position relatively to the nitrogen. The position of the amino-group is not known with certainty, but the formula is probably represented by II (Trans., 1897, 71, 1083).

It will be noticed that the fusing points of these isomerides very closely approach each other. The compound now described melts at almost exactly the temperature given for (3), whilst (2) melts at a temperature only very slightly lower. The authors, however, have satisfied themselves that these substances are not identical. The new aminotrichloropyridine yields a well-defined platinum salt, and (3) does not. Again, the new compound differs from (2), in that it does not yield a precipitate with bromine water in the manner described by Stokes and Pechmann (loc. cit.), and further, it is very unlikely that if (2) had been capable of forming a platinum salt, the fact would have been overlooked.

Although (2) and (3) are so similar in properties, both melting practically at the same temperature and neither forming a compound with platinic chloride, their identity is out of the question, since it has been shown by Stokes and Pechmann (loc. cit.), and by the authors (Trans., 1898, 73, 777) that the parent substance of (2), glutazine, has an amino-group in the γ -position relatively to the nitrogen, whilst (3) was derived from $a\alpha'\beta\beta'$ -tetrachloropyridine, in which the γ -position is undoubtedly occupied by a hydrogen atom.

The method of formation of the new aminotrichloropyridine is of considerable interest. The only possible source of the nitrogen of the amino-group must have been a pyridine nucleus, since pyridine was the only substance containing nitrogen which had been introduced into the flask at any stage. It is noteworthy that the presence of the compound could not be detected in the strongly acid liquor (p. 982), and was recognised only after steam distillation from a strong solution of sodium carbonate. Further, it has been shown by many reactions (Trans., 1898, 73, 777) that the substitution of chlorine by the aminogroup, in the class of compounds under consideration, does not take place with any great readiness, except at temperatures considerably above 100°, and it is therefore impossible that the production of this aminotrichloropyridine can be due to the liberation of ammonia in a current of steam, by the action of sodium carbonate, from any possible ammonium compound formed by the breaking down of the pyridine ring, and the subsequent action of the ammonia so formed on a tetrachloropyridine. From these considerations, the only possible conclusion that can be drawn is that the antecedent of this substance is a compound in which one pyridine nucleus is united through the nitrogen atom with a carbon atom of a second—a compound which, waiving for

the moment the question as to which of the carbon atoms is concerned, would be represented thus:

If this explanation is correct—and in its support the authors believe they have further evidence, which, however, cannot well be offered here—this is the first recorded instance of the existence of a complex of this type.

EXPERIMENTAL.

Dry chlorine was passed into fused, dry pyridine hydrochloride (containing an excess of hydrogen chloride as described in the introduction) at 115—120° during several weeks, until the upper layer disappeared. On cooling, a crystalline mass was obtained. Two methods were adopted in the examination of the products. In the first, the whole was distilled in steam, whilst in the second the crystalline material was separated by means of dry chloroform before steam distillation of the liquid portion was undertaken.

I. The contents of the flask, after chlorination, were distilled in a current of steam without any previous separation, and an oil passed over precisely as in the manner described in Part I. (loc. cit.), the process requiring some days for its completion. The greater part of the contents of the chlorination flask formed an emulsion, gradually darkening in colour to a deep chocolate brown, which, on cooling, settled down as a guttapercha-like cake. The strongly acid mother liquor, on being made alkaline with ammonia, deposited a small crop of colourless crystals, which, on purification from dilute alcohol, melted at 66—67° (uncorr.). The same product was found in much larger quantity in the volatile oil, and is described below (p. 985).

The brown cake was again distilled in a current of steam from a saturated solution of sodium carbonate, when feathery, colourless needles were obtained from the aqueous distillate on cooling. These crystals are readily soluble in acids, and are reprecipitated by alkalis; they dissolve in the usual organic solvents, but are only sparingly soluble in hot, and almost insoluble in cold water. After recrystallisation several times from dilute alcohol, the substance melted at 159—160° (uncorr.), and, on analysis, proved to be a trichloraminopyridine.

0.3224 gave 0.3568 CO₂ and 0.0448 H₂O. C=30.18; H=1.54.

0.3827 , 46.7 c.c. nitrogen at 19° and 764 mm. N = 14.11.

0.2887 , 0.6463 AgCl. Cl = 54.54.

 $C_5NHCl_8\cdot NH_2$ requires C=30.44; H=1.52; N=14.20; Cl=53.83 per cent.

When dissolved in hydrochloric acid and treated with platinic chloride, the platinochloride was obtained in short, thick, golden-yellow needles.

0.4137 gave 0.1005 Pt. Pt = 24.29. $(C_6NHCl_8\cdot NH_9)_{er}H_9PtCl_6$ requires Pt = 24.30 per cent.

The contents of the flask, which were strongly alkaline from the excess of sodium carbonate, after filtration and neutralisation with hydrochloric acid, yielded a precipitate of brown, crystalline matter, very soluble in alkalis, reprecipitated by acids, and moderately soluble in the usual organic solvents. This substance is still under examination, as is also the residue of the steam distillation.

II. In order to avoid the rather considerable amount of decomposition which takes place when the separation is carried out as above described, a modification of this plan was adopted in the later experiments. The solid or semi-solid product of the chlorination was warmed, drained by the aid of the filter pump and washed with chloroform, when a considerable quantity of colourless crystals was left behind. This crystalline separation was purified by several recrystallisations from dry chloroform, dried in a vacuum, and kept in a well stoppered bottle.

It was found that when these crystals were dried in the air they gave off hydrogen chloride for some time after removal to a desiccator. This was doubtless due to interaction with the small amount of moisture absorbed from the air during the process of drying, and does not occur when the substance is dried in a desiccator over sulphuric acid, the crystals in the latter case decreasing in weight by an insignificant amount when left for some days in a vacuum over potash. The compound melted sharply at 187—188° (uncorr.), and gave the following numbers on analysis:

0.7575 gave 0.6050 CO₂ and 0.0155 H₂O. C = 21.72; H = 0.22. 0.2830 , 0.8340 AgCl. Cl = 72.86.

 $C_{10}Cl_{11}HN_2$ requires $C=22\cdot22$; $H=0\cdot18$; $Cl=72\cdot22$ per cent.

It is freely soluble in hot, but only sparingly in cold chloroform, carbon tetrachloride, benzene, or pyridine. On treatment with boiling spirit, an interaction takes place, and very beautiful, highly refractive, colourless crystals are obtained which melt at 171—172° (uncorr.), whilst the mother liquor becomes strongly acid, owing to the production of hydrogen chloride. The same change is brought about on contact with water, but the solid is not taken into solution. Glacial acetic acid dissolves it readily on boiling, with copious evolution of hydrogen chloride, and on cooling deposits the crystals melting at

171—172°. These have the composition expressed by the formula $C_{10}N_2Cl_0HO$.

The presence of hydrogen in the parent substance (m. p. 187—188°) was first attributed to the latter being the hydrochloride of a base, but its occurrence with oxygen in the compound now described was so unexpected, considering the methods of preparation, that numerous analyses were made of specimens from different experiments, and in some cases of relatively large amounts of material, before its existence in the molecule was regarded as placed beyond doubt. The following are typical of the numbers obtained:

A determination of the freezing point of a solution in benzene gave the following numbers:

0.2320 gram lowered the freezing point of 19.59 grams of benzene 0.130° ; Mol. wt. = 445; calculated for $C_{10}N_2Cl_0HO = 484$.

This substance is readily soluble in chloroform, carbon tetrachloride, benzene, or glacial acetic acid, but only sparingly so in alcohol, and is insoluble in water, dilute acids, or alkalis. Strong sulphuric or nitric acid, on warming, dissolves it with decomposition, and in the former case with liberation of hydrogen chloride. From its solution in chloroform, if deposited slowly, it is obtained in lustrous, highly refractive crystals of large size. It can be crystallised from pyridine without decomposition, and therefore is not the hydrochloride of a It is not affected by long-continued boiling with water. The evidence at present is insufficient to decide whether the hydrogen and oxygen in the compound are present as hydroxyl. Its behaviour with phosphorus pentachloride has only partly been examined, but it may be stated that pyridine pentachloride was one of the products, thus showing that the pyridine nucleus still remains. The ease with which the parent substance interacts with liquids containing the OH-group points to the presence of this radicle in the new compound, yet, on the other hand, it may be crystallised unchanged from benzoyl chloride or acetyl chloride.

If the crude cake obtained by draining the contents of the chlorination flask is at once crystallised from alcohol, the first crop of crystals contains another and somewhat similar compound, which, after purification by several recrystallisations from alcohol, glacial acetic acid, or chloroform, melts unchanged at 228° (uncorr.). This substance gave the following numbers on analysis:

0.4115 gave 0.4350 CO₂ and 0.110 H₂O. C = 28.82; H = 0.29.

0.2010 required 0.5814 AgNO₈. Cl = 60.22.

0.1922 gave 0.4635 AgCl. Cl=59.68.

0.2885 ,, 17.3 c.c. nitrogen at 14° and 754 mm. N=6.99. $C_6N_2Cl_7HO$ requires C=29.07; H=0.25; Cl=60.00; N=6.78 per cent.

This product is isolated in very much smaller quantity than the preceding one. It is dissolved by the same solvents, but to a less extent. It is probably formed by the interaction of water with a substance of the formula $C_{10}N_{\circ}Cl_{\circ}H$, which has not been isolated.

The authors are not at present prepared to put forward any constitutional formulæ for these compounds, but the investigation is being pursued, and several interesting derivatives have been obtained. This branch of the subject, however, is reserved for a future communication.

The oily filtrate separated from the crystalline products of the chlorination was freed from chloroform and distilled in a current of steam until nothing further was carried over. The residue, which varied between 5 and 10 per cent. of the total weight of material obtained, was in the form of a light, reddish-brown resin very soluble in chloroform or glacial acetic acid, but only sparingly so in alcohol, and insoluble in water. It is very rich in chlorine, but so far no crystalline products have been obtained from it.

The oil volatile in steam, which was obtained from all the experiments in only slightly varying quantities, was treated in the manner described in Part I. (loc. cit.) for the separation of the chloropyridines. It differs very considerably in composition from the product of the action of phosphorus pentachloride on pyridine, as might be expected in view of the difference in the material employed and the conditions under which the chlorination was carried out. The constituents which do not form compounds with mercuric chloride are present in insignificant proportion, whereas in the former case they reached approximately 50 per cent. of the total weight of oil obtained. From this oil, the only crystalline product is pentachloropyridine.

On fractionating the dried oil, separated from the compound with mercuric chloride (*loc. cit.*), the first portion of the distillate was found to consist of a dichloropyridine not obtained in the previous work. This compound, which is formed in fair amount, was purified by dissolving in hydrochloric acid, pouring off from any undissolved oil, reprecipitating with ammonia, and subsequent recrystallisation from

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dilute alcohol, when it was obtained in lustrous, flexible flat needles which melted at $66-67^{\circ}$ (uncorr.). This fusing point agrees with that of the dichloropyridine described by Königs and Geigy (Ber., 1884, 17, 1833) and the identity of the substance was established by the preparation of the mercurichloride (m. p. = 183°, uncorr.) and the platinochloride, the latter of which gave the following numbers on analysis:

0.36 lost, at 100°, 0.019 H_2O and gave 0.0945 Pt. $H_2O = 5.27$; Pt = 26.26.

 $(C_6NH_8Cl_2)_{22}H_9PtCl_6 + 2H_9O$ requires $H_9O = 4.84$; Pt = 26.48 per cent.

The second fraction of the distillate, which was small in amount, consisted of an oil which remained liquid in a freezing mixture of ice and salt. The third fraction, constituting 90 per cent. of the weight of the oil, was redistilled, and the portion boiling between 135—137° under 24 mm. pressure was collected separately. This consisted of the tetrachloropyridine melting at 21—22°, and amounted to upwards of 70 per cent. of the total yield of chloropyridines. Large quantities of this substance have now been obtained and the authors hope to be able to work out its constitution.

As in the former series of experiments (Part I.), the yield of pentachloropyridine is a good one. This substance is chiefly found in the last portions of the steam distillate, which were always collected separately, but is invariably present in the oil separated by treatment with mercuric chloride, and was obtained from it as described in the former paper.

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XCVI.—Homocamphoronic and Camphononic Acids.

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The a-mono-derivatives of camphor are, as a rule, very readily converted into camphoric acid on treatment with oxidising agents such as nitric acid or potassium permanganate, and it is generally accepted

that the change is merely one of conversion of the group <

COOH, unattended by alteration of the structure of the rest of the molecule.

The mode of degradation of the β -halogen derivatives of camphor is quite different from that of the α -derivatives, and the study of the reactions of the products obtained from them, in a manner apparently equally simple, leads to conclusions which, at present, are difficult to entirely reconcile with those drawn from the study of the compounds obtained from camphoric acid. Any new observations as to the manner in which the breaking down of the nuclei may occur can hardly fail, therefore, to be of importance, especially when the changes involved occur at fairly low temperatures, and are effected by agents unlikely to produce violent and deep-seated changes.

Between the a-mono- and the a-di-derivatives of camphor, a remarkable difference in stability is manifested. The former, as mentioned above, are readily oxidised, whilst the di-derivatives are attacked by the ordinary oxidising agents only with great difficulty; thus, a-dibromocamphor is not appreciably affected by ordinary nitric acid (sp. gr. 1·42), although it is attacked by hot, fuming nitric acid (sp. gr. 1·50), and by still stronger acid (sp. gr. 1·52) at the ordinary temperature, whilst aa-nitrobromo- and nitrochloro-camphor are apparently not attacked even by the strongest acid.

This great stability of the a-di-derivatives is of considerable interest, and their oxidation by mild agents might be expected to afford interesting results. Oxidation products of a-dibromocamphor have already been obtained by Kachler and Spitzer (Monatsh., 1883, 4, 554) and by Forster (Trans., 1896, 69, 36), but in both instances use was made of fuming nitric acid, which involved violent action and the consequent possibility of changes too profound to afford a basis for trustworthy conclusions.

Kachler and Spitzer obtained what they concluded to be camphoronic acid and isocamphoronic acid, together with a substance to which they assigned the provisional formula $C_{24}H_{33}BrN_4O_{12}$, whilst admitting its possible want of purity. Forster employed somewhat stronger acid, and found that interaction occurred spontaneously; the product obtained, dibromocampholid, was a lactone which, on reduction, yielded bromocamphorenic acid, $C_{10}H_{15}BrO_2$, and finally, camphorenic acid, $C_{10}H_{16}O_2$, a monocyclic, unsaturated isomeride of campholenic acid. The nature of the changes by which dibromocampholid is produced is not quite clear, however, and it is even probable that the bromine atoms are no longer both attached to the carbon atom with which they were associated in the parent substance.

In view of the interest attaching to the fact that dibromocamphor does not afford camphoric acid as a normal oxidation product, the authors have made numerous experiments with the substance in the hope that it could be oxidised by a method sufficiently mild to give results which would be trustworthy from a theoretical point of

view, and it was found that, whilst dibromocamphor is scarcely affected by agents such as dilute solutions of potassium permanganate, chromic acid mixture, or ordinary nitric acid, it could be readily oxidised by dilute nitric acid if silver nitrate were present in the solution. It is curious that the greater portion of the substance is merely reduced under these circumstances, but a small amount is converted into acid compounds.

The investigation of the products formed under these conditions was carried out with especial care, in order to determine whether camphoronic and isocamphoronic acids were normal oxidation products of dibromocamphor, as the production of the latter acid seemed so very improbable in view of what is now known of its constitution and of that of a-dibromocamphor.

Our results indicated that isocamphoronic acid was not present, but that an acid was formed which might easily be confused with it on superficial examination; this product had the formula $C_{10}H_{16}O_6$, and a study of its properties showed that it was probably identical with the acid of that formula obtained by Forster (Trans., 1896, 69, 49) by the oxidation of bromocamphorenic acid with potassium permanganate, and which had been briefly described by him. On communicating to Dr. Forster our first suspicion as to its identity, he was kind enough to state his readiness to allow us to continue our investigation of its properties, and we take this opportunity of expressing our indebtedness to him for leaving in our hands the study of this interesting substance.

Forster concluded, from an analysis of a silver salt, that the acid was probably dibasic, but we have found that, although a salt having approximately the composition of the one obtained by him is formed if litmus is used as indicator, it is possible under other conditions, notably when phenolphthalein is used to determine the point of neutrality, to prepare a salt whose composition indicates that the acid is tribasic: a view which is confirmed on other grounds, as, for example, by the composition of its iron, copper, and lead salts, and the acid nature of the anhydro-acid which may be easily obtained from it. We propose for this acid the name homocamphoronic acid, in view of the fact that we have obtained camphoronic acid from it in a manner indicating that its constitution may be represented by replacing a -COOH group in camphoronic acid by -CH₂• COOH.

Homocamphoronic acid readily loses water, yielding an anhydro-acid, $C_{10}H_{14}O_5$, from which the original substance may be regenerated by treatment with water or alkalis. The anhydro-acid at once dissolves in a cold, dilute solution of sodium carbonate, producing effervescence, and therefore still contains a carboxyl group.

Marsh and Gardner's camphoic acid resembles homocamphoronic

acid in many ways; that substance has two of its carboxyl groups attached to the same carbon atom, and as a result its anhydro-acid loses carbonic anhydride when heated, yielding camphopyric anhydride, C₉H₁₉O₈ (Trans., 1896, 69, 78). On subjecting the anhydride of homocamphoronic acid to similar treatment, it was found that carbonic anhydride was also eliminated, and that a product having the formula This, however, was entirely different in $C_0H_{14}O_0$ was obtained. character from camphopyric anhydride, as when heated with alkalis it was not altered; moreover, it was acid, and dissolved at once in a dilute solution of sodium carbonate. On closer examination, the substance proved to be a monobasic ketonic acid, and from its formula was evidently a closed chain compound; the nature of the decomposition by which it is formed is therefore exactly similar to that which occurs when dihydrocamphoric acid is distilled (Crossley and Perkin, Trans., 1898, 73, 27), whereby a closed chain ketone is produced from an open chain dicarboxylic acid, and is analogous to the formation of ketopentamethylene from adipic acid by the distillation of its calcium salt.

$$\begin{array}{ll} \mathrm{CH_2 \cdot CH_2 \cdot COOH} \\ \mathrm{CH_2 \cdot CH_2 \cdot COOH} \end{array} = \begin{array}{ll} \mathrm{CH_2 \cdot CH_2} \\ \mathrm{CH_2 \cdot CH_2} \\ \end{array} > \mathrm{CO + H_2O + CO_2}. \end{array}$$

For purely theoretical reasons, we were at this stage led to surmise that the ketonic acid had the structure

and therefore probably contained its carbon atoms in exactly the same position as that of nine out of the ten atoms of camphoric acid, as a glance at the formulæ of Bredt or Perkin will show. It was therefore necessary to inquire whether this aubstance could not be obtained directly from camphoric acid in a simple manner, as such a fact would confirm in a striking manner the formula above suggested for the acid, and also to firmly establish the view that camphoric acid must have the structure represented by one of the three formulæ

On examining the literature, it was found that J. Walker had obtained a very similar substance as a bye-product in the electrolysis of ethylic allocamphorate (Trans., 1896, 69, 755). Dr. Walker kindly sent us a small specimen of his substance, and en comparing directly

the two acids and their parabromophenylhydrazones, it was found that they were identical in all respects.

In view of the importance which this acid now assumes in its relation to the camphor problem, Dr. Walker has agreed to the name camphononic acid which we propose to use for it, and which was chosen in view of the fact that it is isomeric with pinononic acid, a substance obtained by Wagner on oxidising pinene (Ber., 1896, 29, 881). Walker did not examine the degradation products of camphononic acid, but we have been able to effect its oxidation almost quantitatively by the use of very dilute nitric acid, and to prove that camphoronic acid is not only the main product, but is formed to the exclusion of all but a trace of any other acid. This observation establishes that, without doubt, camphononic acid has one of the two formulæ above suggested, and the non-production of any appreciable quantity of other oxidation products would appear to point to the

formula $CH_2 \cdot CH_2$ CMe COOH as the more probable of the two; the production of camphoronic acid would then be expressed as follows:

$$\begin{array}{cccc} \text{CO--CMe}_2 & & \text{CMe}_3 \cdot \text{COOH} \\ \mid & \text{CMe} \cdot \text{COOH} & \rightarrow & \text{CMe} \cdot \text{COOH} \cdot \\ \text{CH}_2 \cdot \text{CH}_2 & & \text{CH}_2 \cdot \text{COOH} \end{array}$$

The two possible formulæ for homocamphoronic acid are easily deduced from those of camphononic acid; they are

$$\begin{array}{lll} CMe_2 \cdot COOH & CMe_2 \cdot CH_2 \cdot COOH \\ CMe \cdot COOH & and & CMe \cdot COOH \\ CH_2 \cdot CH_2 \cdot COOH & CH_2 \cdot COOH \\ \end{array},$$

the corresponding formulæ for anhydrohomocamphoronic acid being probably

$$\begin{array}{ccccc} \text{CMe}_2 \cdot \text{CO} & \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{COOH} \\ \text{CMe} - \text{CO} & \text{and} & \text{CMe} \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH} & \text{CH}_2 \cdot \text{CO} \end{array}$$

The formation of camphononic acid from these, necessitating as it does the closure of the adipic chain, must involve hydrolysis of the succinic anhydride residue, an occurrence which is not difficult to understand. The change may possibly then be represented, using the former of the above structures, as follows:

The fact that homocamphoronic acid yields camphononic acid in this

way is, altogether apart from the formation of camphoronic acid, sufficient to establish the assumption that the former is a substituted adipic acid, and cannot be represented by the structure

in which the longest chain is that of a glutaric acid. This point has been repeatedly discussed by various chemists [compare Perkin and Crossley (Trans., 1898, 73, 6); Bredt and Rosenberg (Annalon, 1896, 289, 13); and Wislicenus (ibid., 1893, 275, 309)], and does not at present call for further remark.

The relationship of camphononic acid to camphoronic acid requires further consideration. Walker (loc. cit.) suggests that camphononic acid is genetically related to camphanic acid, and there is every probability in favour of this view. Camphanic acid is obtained from bromocamphoric acid by treatment with water, and also by the direct oxidation of camphoric acid. There is no sufficient reason to imagine that the bromination of camphoric acid does not follow the general rule; moreover, Fittig has shown that when acids are oxidised, it is the hydrogen in attachment to a tertiary carbon atom which is replaced by hydroxyl, and there is every reason to believe that in camphoric acid, the only tertiary carbon atom is that to which carboxyl is attached. From both points of view, therefore, it is to be surmised that the intermediate hydroxy-compound would contain the grouping: $-CH_2-\dot{C}(OH)\cdot COOH$, and the change to camphononic acid would be represented in a simple manner, thus:

If this is the true view of the mode of origin of camphononic acid, the ketonic group of this substance must represent the >OH·COOH group of camphoric acid, and thus afford evidence in favour of the rejection of the Perkin-Bouveault formula. To establish the relationship between the two substances ought to be a comparatively simple matter. Unfortunately, all experiments in this direction, conducted with a view to the production of camphanic acid from camphononic acid, and vice versa, have so far been fruitless; they are still being carried on, however, in the hope that we may obtain evidence with regard to this important point.

EXPERIMENTAL.

Oxidation of a-Dibromocamphor with Nitric Acid in presence of Silver Nitrate.

a-Dibromocamphor in presence of silver nitrate may be oxidised with great ease by nitric acid, even when the acid is quite dilute (1 in 3). Although rapid oxidation occurs under these conditions, many experiments were made before any definite oxidation produced was isolated, and the best results were obtained by working on the line followed by Kachler and Spitzer (loc. cit.) in isolating the products which they concluded to be camphoronic and isocamphoronic acids. The following is an account of an experiment made with a view to determine whether these acids were present in the product obtained by the new process.

A solution of silver (70 grams) in nitric acid (400 grams of acid, sp. gr. 1·42) was heated in a flask on the water-bath and successive small quantities of dibromocamphor (100 grams) were added; after each addition, nitrous fumes were rapidly evolved, and the action was allowed to moderate before more substance was added. The oxidation was continued during about 6 hours; the residual silver was then exactly precipitated by the addition of hydrochloric acid, and the filtrate concentrated by evaporation in a retort, care being taken to get rid of the last trace of nitric acid by repeated dilution and evaporation to dryness in a dish on the water-bath. On adding a considerable quantity of water to the residue, an oily substance separated, as described by Kachler and Spitzer. This gradually solidified and was collected by filtration and examined, the aqueous liquid being worked up separately.

Neutral portion of Oxidation.—The insoluble substance, which weighed about 7—8 grams, had the general properties and practically the same melting point as the substance C₂₄H₃₈BrN₄O₁₂, described by Kachler and Spitzer. On recrystallisation from methylic alcohol, the melting point rose by a few degrees and the substance itself was found to be quite free from bromine; Kachler and Spitzer's specimen was probably impure owing to the presence of some compound containing a high percentage of bromine.

0.1493 gave 0.2561 CO₂ and 0.0752 H₂O. C=46.8; H=5.6.

0.3380 , 31.2 c.c. moist nitrogen at 13° and 756 mm. N = 11.0.

 $C_{10}H_{14}N_2O_6$ requires $C=46\cdot 5$; $~H=5\cdot 4$; $~N=10\cdot 8$ per cent. Kachler and Spitzer found

Br = 12.5; C = 44.0; H = 5.35; N = 9.1 per cent.

The substance was readily soluble in hot methylic and ethylic

alcohols, acetic acid, and ethylic acetate, but less so in benzene and nearly, or quite, insoluble in light petroleum. It crystallised from hot methylic alcohol in beautiful, apparently regular, six-sided plates belonging to the orthorhombic system; and from cold methylic alcohol in large prisms when the rate of evaporation was slow enough. It melted at 93—94°.

It is probably a dinitrolactone, $C_{10}H_{14}(NO_2)_2O_2$, derived from a hydroxy-acid, $C_{10}H_{18}O_3$, and is insoluble in sodium carbonate, but dissolves in hot caustic alkalis, from which it seems to be precipitated on the addition of an acid. By the action of alkali, decomposition undoubtedly takes place to some extent as a considerable quantity of nitrite may be detected in the alkaline liquid.

The substance may be reduced by means of stannous chloride, and after removal of the tin by means of hydrogen sulphide and subsequent evaporation to dryness, a small quantity of a crystalline substance was obtained which gave a yellow, sparingly soluble platinochloride, and therefore contained one or two amido-groups; the quantity obtained, however, was too small for further investigation.

Acid product of Oxidation.—The soluble portion of the oxidation product was made alkaline with baryta water, the resulting slight precipitate removed by filtration, and the filtrate heated to boiling, when a considerable quantity of a white, insoluble salt (a) appeared, and was separated by filtration.

The filtrate was made neutral by careful addition of sulphuric acid, filtered from barium sulphate, and heated with excess of copper acetate, when a copious blue precipitate (b) was produced, and increased in amount as the temperature of the liquid was raised to the boiling point. The precipitate was collected, the copper in the filtrate removed by means of hydrogen sulphide, and the filtrate boiled to expel the excess of the gas; basic lead acetate was then added until the precipitate (c) no longer increased in amount.

The residual liquid gave no further precipitate with any metallic salts, with the exception of mercurous nitrate, which caused the separation of a slight quantity of insoluble matter (d), and after the removal of all metals by means of hydrogen sulphide, was evaporated to dryness. A small quantity of a syrupy acid (s) was left, which yielded crystals only in the course of several months; these were separated and purified by crystallisation from ethylic acetate.

The acid (s) thus obtained is sparingly soluble in ethylic acetate and acetone, but dissolves readily in water; it is nearly insoluble in chloroform and benzene. After crystallisation from dry ethylic acetate, it melts at 190°, and after resolidification melts at the same temperature as before. It gave the following results on analysis:

0.1704 gave 0.3247 CO₂ and 0.0940 H₂O. C = 52.0; H = 6.1. $C_{10}H_{14}O_{8}$ requires C = 52.2; H = 6.1 per cent.

The substance has the properties of a dibasic acid; thus, on titration with N/10 caustic soda in presence of phenolphthalein, the number obtained for its equivalent was 120, that calculated from the formula $C_{10}H_{14}O_6$ being 115.

A solution of the ammonium salt, when fairly strong, gives precipitates with basic lead acetate and with mercurous nitrate, soluble in excess of the reagent in both cases; solutions of neutral lead acetate and barium or calcium chlorides gave no precipitate.

This acid does not appear to be obtained when dilute nitric acid is used as the oxidising agent, and we have not yet succeeded in obtaining it in quantity sufficiently large for close examination.

From the foregoing metallic precipitates, the metals were removed and the acids obtained from them examined. The barium precipitate (b) was suspended in water and treated with exactly the necessary quantity of dilute sulphuric acid, the solution then being filtered and evaporated. After remaining for some weeks, a few prismatic crystals only had made their appearance. As these melted somewhat indefinitely between 145° and 175° , the acid was boiled with excess of baryta water and the precipitated barium salt treated as before. The precipitate was smaller in amount than (b), and the acid obtained from it crystallised almost at once after evaporation. The acid, after recrystallisation, melted at temperatures between 170° and 185° , according to the rate of heating, water being evolved. It gave the following result on analysis:

This acid, although resembling camphoronic acid in some respects, differed from it both in percentage composition and melting point.

The copper precipitate (b), which was supposed to contain iso-camphoronic acid, was suspended in water, decomposed with hydrogen sulphide, and the filtrate evaporated nearly to dryness, when a separation of solid matter soon took place. This was collected and crystallised from water. It formed minute crystals, which melted at about 175—180°, a temperature close to that at which isocamphoronic acid melts. On analysis, it gave the following numbers:

0.2009 gave 0.3828 CO₂ and 0.1197 H₂O. C=51.9; H=6.6 per cent. which do not accord well with those required for isocamphoronic

acid, $C_9H_{14}O_6$. Further investigation showed that the substance is identical, not only with that obtained from the barium precipitate (a), but also with the acids isolated from the precipitate with lead (c) and mercurous (d) salts. The analysis of the acid obtained from the mercurous precipitate gave the following result:

0.1726 gave 0.3270 CO₂ and 0.1025 H₂O. C = 51.9; H = 6.7 per cent.

Homocamphoronic Acid, $C_{10}H_{16}O_6$.

The acid $C_{10}H_{16}O_6$, which we propose to term homocamphoronic acid, is not entirely new, but its true nature has not hitherto been recognised. It will be seen from the foregoing experiment that Kachler and Spitzer probably had this substance in their hands, but if so, that it was confused with camphoronic or isocamphoronic acid, either on account of its resemblance to those acids or to its admixture with them.

It has also been obtained by Forster (Trans., 1896, 69, 49) by oxidising bromocamphorenic acid with ice-cold potassium permanganate solution, and he has given a brief description of its properties. The acid is one of considerable importance, as it has now been demonstrated that it may be obtained from a-dibromocamphor without recourse to any violent mode of treatment.

In order to prepare this acid in fairly large amount, it is necessary to employ nitric acid much weaker than that used in the foregoing experiments. The following method of obtaining it in one step from dibromocamphor may be used: Dibromocamphor (150 grams) is placed in a capacious flask and covered with a mixture of ordinary nitric acid (400 c.c.) and water (600 c.c.) in which silver (115 grams) has been dissolved. The whole is heated gently until oxidation commences, the operation being continued for about three days of eight hours each. If the liquid is allowed to distil over during the process, it is found that a considerable quantity of camphor and monobromocamphor is carried over at the same time. After nitrous fumes cease to be evolved, the excess of silver is precipitated with the requisite quantity of hydrochloric acid, the liquid filtered, and nitric acid got rid of in the usual way. The oily residue is finally diluted with about 20 c.c. of hot water and allowed to cool. The first deposit of insoluble matter is separated by filtration, washed with a little water, and the combined aqueous liquors allowed to remain for a few hours. crystalline matter which separates is collected, dried and washed with chloroform, and finally crystallised from a mixture of acetone and ethylic acetate. In this way, about 4-6 grams of crude homocamphoronic acid are obtained, and a further small quantity may be isolated from the mother liquors by means of lead acetate, the resulting precipitate being decomposed by hydrogen sulphide and the liquid worked up as usual.

Homocamphoronic acid separates from a mixture of acetone and ethylic acetate in the form of small, shimmering, white plates or flattened needles. It dissolves readily in methylic and ethylic alcohol, and is freely soluble in moist ether, but somewhat sparingly soluble in the dry liquid. It is sparingly soluble in dry acetone, still more so in dry ethylic acetate, and nearly insoluble in benzene, chloroform, or light petroleum. It dissolves with great readiness in cold nitric acid and also in hydrochloric acid, and does not separate readily from them. When pure, it is not very readily soluble in cold water.

The melting point of homocamphoronic acid is a little difficult to determine, as it varies greatly with the conditions under which it is taken. When very slowly heated, its melting point may be as low as 170°; if heated in the usual way in a capillary tube, the temperature being raised fairly quickly, it is usually found to be 183—185°; if, however, the capillary tube is plunged into sulphuric acid at 200°, fusion does not occur at once, but only after the lapse of several seconds, and this is the case at any temperature below 206°. At 206—207°, however, it melts immediately the tube is immersed in the hot liquid, and this temperature is probably the true (uncorrected) melting point of the acid. In every case effervescence accompanies the fusion, and the product, if allowed to solidify, is afterwards found to melt at about 87°.

Homocamphoronic acid is a fairly stable substance; it may be boiled with strong nitric acid for several hours without suffering any appreciable change. It dissolves in warm, concentrated sulphuric acid, and when heated with it at a temperature of 200° is converted into the anhydride. It dissolves readily in alkalis and alkali carbonates, and solutions in the latter do not decolorise dilute potassium permanganate even when warm, and may be left in the cold with it for several weeks before appreciable oxidation occurs.

Homocamphoronic acid is optically active. A solution of 0.5064 gram of the substance in 25 c.c. of water examined in a 2 dcm. tube at 17° gave as a mean of 10 concordant readings, $a_0 = -1^\circ$ 25′, whence $[a]_0 = -10.28^\circ$.

The basicity of homocamphoronic acid was for a long time very doubtful. Forster concluded, from an analysis of its silver salt (Ag=51.78 and 51.87 per cent.), that the acid was probably dibasic. We have confirmed the number he obtained for the silver salt prepared in this way:

0.1519 gave 0.0790 Ag. Ag = 52.0.

 $C_{10}H_{14}O_6Ag_2$ requires Ag = 48.7 per cent. $C_{10}H_{13}O_6Ag_3$, Ag = 58.6 ,

These results are intermediate between those required for a dibasic and a tribasic acid. In view of the doubtful nature of the silver salt, the following experiments were made:

The barium salt, prepared by boiling an aqueous solution of the acid with excess of barium carbonate and evaporating the filtrate, did not crystallise; the salt, dried at 150°, gave Ba = 38.8 per cent., that required for $C_{10}H_{14}O_6Ba$ being 37.3, and for $(C_{10}H_{18}O_6)_2Ba_8$ being 47.2 per cent. On the other hand, the salt obtained by adding excess of barium hydroxide to the aqueous solution of the acid, precipitating the excess of barium by passing carbonic anhydride through the hot solution, filtering and evaporating, gave Ba = 43.0 per cent. results point to the acid being tribasic. Moreover, on titration with sodium hydroxide, using litmus as the indicator, it behaved almost exactly as a dibasic acid, the equivalent found being 110 as against 116, the calculated value, whilst, with phenolphthalein as indicator, the number obtained was 78.0, that calculated for a tribasic acid being 77.3. The behaviour of the acid in this respect is therefore similar to that recorded by Lean (Trans., 1894, 65, 995) and by Kipping (Trans., 1896, 69, 954) in the cases of substituted butanetetracarboxylic acids and camphotricarboxylic acids respectively, and recalls the fact that the basicity of camphoronic acid was for a very long time uncertain.

That homocamphoronic acid is tribasic, is confirmed by the following analyses of salts, made by using a solution of the acid neutralised with soda, and phenolphthalein as indicator.

The silver salt is not precipitated at once in very dilute solution, but separates as a jelly-like mass on adding a large excess of silver nitrate. It was filtered and washed, first with water, then with alcohol and ether, and dried in a vacuum.

0.2312 gave 0.1341 Ag. Ag = 58.0. $C_{10}H_{18}O_6Ag_3$ requires Ag = 58.6 per cent.

The lead salt, obtained by adding lead acetate to a solution of the acid or of its sodium salt, forms an amorphous, white precipitate, and is insoluble in acetic acid, but dissolves readily in dilute nitric acid.

0.1165 gave 0.0986 PbSO₄. Pb = 57.8. $(C_{10}H_{13}O_a)_{2}$ Pb₈ requires Pb = 57.8 per cent.

The copper salt is obtained on adding copper acetate to the solution of the normal sodium salt, and forms a sparingly soluble, bluish-

green, amorphous precipitate. A specimen dried at 100° gave the following result on analysis:

0.3270 gave 0.1177 CuO. Cu = 28.7. $(C_{10}H_{18}O_5)_2Cu_3$ requires Cu = 29.2 per cent.

A solution of the normal sodium salt yields a bulky, buff precipitate with ferric chloride, and a voluminous, white precipitate with mercurous nitrate; the latter also produces a precipitate in the solution of the acid. Zinc sulphate yields a white precipitate with the hot solution. Salts of magnesium, calcium, barium, strontium, bismuth, and the other common metals give no precipitate, but the normal barium salt is formed when a strong solution of the acid in a slight excess of baryta water is heated to boiling; the precipitate, however, is not so copious as that obtained when camphoronic acid is treated in the same manner.

Anhydrohomocamphoronic Acid,
$$COOH \cdot C_7H_{18} < CO > O$$
.

When homocamphoronic acid is boiled with acetyl chloride, it is gradually dissolved, and hydrogen chloride is continuously evolved. After several hours, when most of the acid has disappeared, the liquid is filtered, and the acetyl chloride got rid of by evaporation in a dish on the water-bath; the dish is then placed in a vacuum over caustic potash, and in the course of a few days the mass solidifies, and may be purified by trituration with a little benzene, and crystallisation from the same liquid.

The easiest mode of preparing the anhydro-acid, however, consists in heating the substance at 180° until the effervescence due to the escape of water vapour has ceased. Chloroform is then added, the whole heated to boiling, filtered, and shaken two or three times with small quantities of water, dried, and evaporated; the residue is then crystallised from benzene.

The substance may also be made by warming homocamphoronic acid with sulphuric acid for a few minutes, and, on the addition of water to the cold solution, is precipitated as an amorphous mass, which may be washed, dried in a vacuum, and crystallised from benzene.

Anhydrohomocamphoronic acid crystallises from benzene in flat needles or prisms which melt sharply at 86—87°. It dissolves very readily in ethylic acetate, methylic and ethylic alcohols, chloroform, and acetic acid, more sparingly in benzene, and is nearly insoluble in light petroleum. A specimen crystallised from chloroform and dried in a vacuum gave the following result on analysis:

0.2037 gave 0.4185 CO₂ and 0.1184 H₂O. C=56.0; H=6.4. $C_{10}H_{14}O_5$ requires C=56.1; H=6.5 per cent.

Anhydrohomocamphoronic acid has the properties of a carboxylic acid, and when placed in a cold dilute solution of sodium bicarbonate quickly dissolves, carbonic anhydride being liberated. It dissolves very rapidly in cold alkalis, and if an acid is at once added to the solution, the precipitate is found to contain unchanged anhydro-acid; if, however, a few minutes are allowed to elapse before the addition of acid, no immediate precipitate is caused, but homocamphoronic acid separates on scratching the tube with a glass rod. Hydrolysis may also be effected by heating the substance with water for several hours, or by boiling it for a short time with dilute hydrochloric or sulphuric acids.

The stability of the anhydro-acid is very remarkable; thus, it may be heated for a short time with strong sulphuric acid until the latter begins to evolve white fumes without suffering appreciable change, and the solution does not darken in colour; on adding water to the cooled liquid, the anhydro-acid separates unchanged.

Homocamphoronamilic acid, $C_6H_5\cdot NH\cdot CO\cdot C_7H_{18}(COOH)_9$, is easily prepared by dissolving the anhydro-acid in a little benzene and adding to the hot solution the calculated amount of aniline; cloudiness at once ensues, and an oil separates which quickly becomes crystalline if the liquid is boiled for a few moments. The hot liquid is filtered and the product washed with dilute hydrochloric acid, dried on porous porcelain, then dissolved in ethylic acetate in which it is readily soluble; to the solution benzene is then added until slight precipitation occurs. The substance separates in white needles which melt with effervescence at 98—100°. After exposure over sulphuric acid in a vacuum, a specimen was added with the following results:

0.1667 gave 0.3840
$$CO_2$$
 and 0.1009 H_2O . $C = 62.8$; $H = 6.7$. $C_{16}H_{21}NO_5$ requires $C = 62.5$; $H = 6.8$ per cent.

Homocamphoronanilic acid is sparingly soluble in chloroform and benzene, and practically insoluble in petroleum; it is nearly insoluble in cold water, but dissolves in cold dilute sodium carbonate solution, and is reprecipitated on the addition of acid.

The paratolilic acid, $C_{17}H_{23}O_6N$, obtained by substituting paratoluidine for aniline in the process just described, is a more characteristic substance than the anilic acid. It crystallises in beautiful, glistening needles from a mixture of ethylic acetate and benzene on addition of petroleum, melts with effervescence at $163-164^\circ$, dissolves somewhat sparingly in ethylic acetate, benzene, or chloroform, and is insoluble in light petroleum. A specimen dried at 100° gave the following result on analysis:

0.2027 gave 0.4683 CO_2 and 0.1350 H_2O . C = 63.0; H = 7.4. $C_{17}H_{28}O_2N$ requires C = 63.5; H = 7.2 per cent.

Action of Heat on Homocamphoronic Acid. Formation of Camphononic Acid.

Anhydrohomocamphoronic acid, in quantity not exceeding 1 gram, is heated in a test tube in a fusible metal bath until brisk effervescence sets in; it gradually darkens in colour and oily drops appear on the side of the tube. After about one minute, the tube is allowed to cool; a little chloroform is then added and boiled in order to wash down the acid from the side of the tube. The chloroform is afterwards boiled off, and the residue again heated until the condensed acid solidifies immediately on the cool portion of the tube. A number of tubes prepared in this way are washed out with boiling benzene, and the combined liquids, after filtration, are evaporated to a small bulk. Hot light petroleum is then added to the boiling liquid until permanent turbidity ensues; the flask is shaken to cause the oil to adhere to the side of the vessel, and the liquid poured out into a beaker and allowed to cool, when the ketonic acid separates as a paste of minute, fern-like crystals.

When the decomposition has been incomplete, it is usually difficult to separate the unaltered anhydrohomocamphoronic acid by crystallisation, and it is necessary to proceed as follows. The crude acid is boiled with excess of soda for about 15 minutes, a distinct odour of peppermint becoming noticeable; the cooled liquid is twice extracted with chloroform to remove neutral products, acidified with hydrochloric acid, evaporated to dryness, and the residual mass extracted with chloroform to remove the soluble ketonic acid from any homocamphoronic acid produced by hydrolysis of its anhydride. The substance may be crystallised from a mixture of benzene and light petroleum, as recommended above.

Camphononic acid is very readily soluble in chloroform, acetic acid, methylic and ethylic alcohols, ether, and ethylic acetate, readily also in benzene and hot water, less so in cold water, and very sparingly so in light petroleum. It crystallises from benzene, or a mixture of benzene and chloroform, in fern-like crystals, and from dilute acetic acid in curious, long needles, which are apparently striated prisms, but consist of aggregates of opaque, flattened needles. It begins to separate from a small quantity of hot water as an oil, but the solution soon deposits small needles. When heated, it begins to volatilise slowly at about 205°, melts sharply at 228°, and boils and becomes brown at about 255°. A specimen crystallised from ethylic acetate and dried at 100° gave the following results on analysis:

Camphononic acid is scarcely altered by warming with strong sulphuric acid at 150°. It does not suffer appreciable change when boiled with strong soda, although a faint odour of peppermint may usually be detected. It may be boiled with fuming hydrochloric acid for several hours without undergoing change, and crystallises from the cooled liquid in beautiful, fern-like crystals. The alcoholic solution gives no coloration with ferric chloride.

The acid is saturated: the coloration produced by the addition of a drop of bromine to its solution in chloroform is not discharged, even after several minutes, although it gradually disappears when the solution is warmed, hydrogen bromide being evolved; moreover, a solution of the acid in sodium bicarbonate does not discharge the colour of a dilute solution of potassium permanganate within several days, although reduction of the permanganate occurs fairly rapidly on warming.

The specific rotatory power of a solution of 1.075 grams of camphononic acid in 70 c.c. of ethylic acetate was determined in a 2 dcm. tube at 16° ; the mean of ten concordant readings gave $a_D = +0^{\circ} 40' 30''$, whence $[a]_D = +21.97^{\circ}$.

The equivalent of camphononic acid was determined by titration against standard caustic soda, phenolphthalein being used as indicator; the number obtained was 170, or exactly that required for a monobasic acid, $C_0H_{14}O_8$.

It has been stated that camphononic acid is identical with the ketonic acid obtained by Walker from camphoric acid, and the following observations made with the acid, and the specimen kindly supplied by Dr. Walker served to establish the point. The substances melted simultaneously at 228°, as did an intimate mixture of the two; both acids sublimed in capillary tubes at temperatures considerably below their melting point, and the sublimates had exactly the same characteristic appearance under the microscope. A careful examination of the two acids in polarised light under various conditions revealed no difference. Moreover, a portion of each acid was converted into the parabromophenylhydrazone, and these were compared, with the result that no difference could be detected between them.

The phenylhydrazone, COOH·C₈H₁₈:N·NH·C₆H₅, is obtained by warming a solution of camphononic acid in dilute acetic acid with one of phenylhydrazine acetate for half an hour; on adding water, a brownish, tarry mass was precipitated, which was collected and crystallised from a small quantity of acetic acid. The whole was spread upon unglazed earthenware, and when dry was crystallised from chloroform. The hydrazone separated in nearly colourless needles and melted sharply at 174° . A specimen dried at 100° was analysed.

0.1703 gave 0.4336 CO₂ and 0.1211 H₂O. C = 69.5; H = 7.8. $C_{15}H_{20}N_2O_2$ requires C = 69.3; H = 7.7 per cent. VOL. LXXV.

The hydrazone is readily soluble in ethylic acetate and formate, moderately so in ethylic alcohol, and crystallises from the latter in long, slender needles. It dissolves very readily also in strong formic and acetic acids. It is less soluble in benzene, especially when cold, and apparently insoluble in light petroleum. It still retains acid properties, dissolves in sodium carbonate, and is reprecipitated apparently unchanged on the addition of an acid to the solution.

The parabromophenylhydrazone, COOH·C₈H₁₈:N·NH·C₆H₄Br, is readily obtained by dissolving the acid in a small quantity of cold acetic acid, adding a cold solution of parabromophenylhydrazine acetate in acetic acid, and finally water, until faint turbidity occurs. The mixture is gently warmed, when, as a rule, nearly the whole of the acid separates as the hydrazone in the form of beautiful, glistening needles. It is sparingly soluble in acetic acid and separates from the hot liquid in transparent, four-sided needles or prisms, which probably belong to the monoclinic system, and are truncated at each end by two smaller faces. It melts to a brown liquid at 194°. A specimen prepared in this way was dried at 100° and analysed.

0.1980 gave 0.1102 AgBr. Br = 24.2. $C_{18}H_{19}O_{2}N_{2}Br$ requires Br = 23.7 per cent.

The substance is much less soluble in most solvents than the phenylhydrazone. It is somewhat sparingly soluble in cold chloroform, and a hot saturated solution deposits the substance in the form of silky needles or glistening prisms. It is nearly insoluble in cold benzene, but dissolves readily in hot ethylic acetate.

The semicarbazone, $C_9H_{14}O_2N\cdot NH\cdot CO\cdot NH_2$, is not so readily obtained as the hydrazones. It is best made by adding to a solution of the ketonic acid, dissolved in a little methylic alcohol, a solution of semicarbazide hydrochloride and the calculated quantity of sodium acetate in the smallest possible quantity of water. The whole is warmed at $70-80^\circ$ for about 2 hours, and then allowed to remain in a cool place. The substance separates in the form of very long, transparent needles, and may be separated and recrystallised from a small quantity of dilute methylic alcohol. It is not very readily dissolved by methylic alcohol, but tends to form supersaturated solutions in that liquid. It is insoluble in cold benzene and chloroform, vary sparingly soluble in cold ethylic acetate, but more readily soluble in ethylic formate. It crystallises in beautiful, well-formed prisms from dilute methylic alcohol, and melts and decomposes at $230-231^\circ$.

Oxidation of Camphononic Acid.

Camphononic acid is not advantageously oxidised by means of potassium permanganate or chromic acid, and it was found that dilute

nitric acid was the most convenient agent, the following method being found to afford the best results. Camphononic acid was dissolved in about ten times its weight of water and the whole heated to boiling under a reflux condenser on the sand-bath. To the hot mixture was then added small quantities of nitric acid which had been diluted with water and boiled to remove nitrous fumes. When oxidation commenced, the addition of nitric acid was interrupted; when brown fumes had disappeared more nitric acid was added, the process being continued so long as any effect was produced. The liquid was then evaporated to remove nitric acid, and the residue was dissolved in cold water, made alkaline with cold baryta water, and filtered. The filtrate was heated to boiling, when a copious precipitate was produced; this was collected, the liquid carefully neutralised, and lead acetate solution added to it drop by drop, the small quantity of precipitate produced being separated by filtration. The liquid, after removal of the lead and barium, left practically no residue on evaporation. On getting rid of the metals from the two precipitates, the acids set free crystallised fairly quickly, and their solutions, when left, solidified almost completely, and were spread upon porous earthenware to absorb the small quantity of syrupy mother liquor; this was afterwards extracted by prolonged treatment with boiling water, and afforded a further small quantity of the same product. Practically one acid only was obtained by oxidising camphononic acid in the above manner.

The whole of the crystalline product was collected and crystallised from a little ethylic acetate; the substance separated in minute needles, which melted at temperatures dependent on the manner in which the observation was made. Thus, if very slowly heated, it melted sometimes as low as 145°, but if the temperature was raised fairly rapidly in the usual manner, the melting point rose to 158—159°, whilst if the capillary tube was plunged into acid at 160°, fusion did not occur until a temperature several degrees higher had been reached. After solidification, the product melted at temperatures between 100° and 130°. The acid, dried in a vacuum, gave the following result on analysis:

0.2003 gave 0.3640 CO₂ and 0.1204 H₂O. C = 49.6; H = 6.6. $C_9H_{14}O_6$ requires C = 49.5; H = 6.5 per cent.

In properties and composition the acid agrees closely with camphoronic acid, and the identity of the two was confirmed by preparation from the oxidation product of the anhydro-acid and the anilic acid, which melted at 136° and 147° respectively (compare Perkin and Thorpe, Trans., 1897, 71, 1192). The ammonium salt gave no precipitate on addition of barium chloride, but when the solution was

made alkaline with ammonia and boiled, a copious precipitate was deposited. The solution of the acid rendered faintly alkaline by addition of milk of lime, gave a precipitate when boiled, and the free acid, on addition of lead acetate, gave a white precipitate which was insoluble in dilute acetic acid.

The product of oxidation of camphononic acid with dilute nitric acid, appears, therefore, to consist almost entirely of camphoronic acid.

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XCVII.—The Action of Hydrogen Peroxide on Secondary and Tertiary Aliphatic Amines. Formation of Alkylated Hydroxylamines and Oxamines.

By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING, B.Sc.

In a recent paper (Trans., 1899, 75, 792), the authors have given an account of the reaction of alkyl haloids with hydroxylamine. They have shown that methylic iodide and hydroxylamine react, forming trimethylamine oxide, or trimethyloxamine, (CH,), N:O, whilst ethylic iodide forms at first β-diethylhydroxylamine, (C,H,),N·OH, and, by further action, tristhyloxamins, (C₂H₅)₃N:O. Similarly, β-dipropylhydroxylamine and \(\beta\)-di-isopropylhydroxylamine are formed by the reaction of hydroxylamine with propylic and isopropylic iodide respectively; the corresponding oxamines have not yet been obtained by this method. The constitution assigned by us to these oxamines, as isomerides of the trialkylated hydroxylamines, suggested the possibility that they might be produced by the direct oxidation of the corresponding trialkylated amines, of which they may be regarded as the oxides. Moreover, it seemed likely that even substituted hydroxylamines might be produced by the direct oxidation of primary and secondary amines. The authors have shown ground for the supposition that the production of trialkylated oxamines, R.N:O, is probably preceded by the formation of the corresponding trialkylated hydroxylamines, R. N. OR, which, being unstable, at once change into the isomeric oxamines. Moreover, they have proved that the first product of the action of ethylic iodide on hydroxylamine is not diethyloxamine, but diethylhydroxylamine.

Experiment has shown that this direct oxidation of the amines may be effected by means of hydrogen peroxide. In this way, trimethylamine, triethylamine, and tripropylamine have been converted into the corresponding examines, whilst diethylamine has been converted into β -diethylhydroxylamine, an example of the direct exidation of a residue of ammonia into one of hydroxylamine, and, similarly, dipropylamine has been directly exidised into β -dipropylhydroxylamine.

The method is, doubtless, capable of further extension to the direct oxidation of other nitrogen compounds, and the authors have already made a number of preliminary experiments in this direction. It has not been found possible, however, by direct oxidation to convert a primary amine into a mono-alkylated hydroxylamine, and all experiments made with the view of directly converting ammonia into hydroxylamine have failed. So far, it appears that hydrogen peroxide is capable of adding one atom of oxygen to the nitrogen of tertiary amines, and of converting the hydrogen atom of secondary amines into a hydroxyl group.

As has been pointed out in a previous paper (loc. cit.), the alkylated oxamines closely resemble in their properties the dimethylaniline oxide which has been recently prepared by Bamberger and Tschirner (Ber., 1899, 32, 3421), by acting on dimethylaniline with hydrogen peroxide. On the other hand, they differ considerably from the alkylpiperidine oxides described by Wernick and Wolffenstein (Ber., 1898, 31, 1553; 1899, 32, 688) as resulting from the action of hydrogen peroxide on alkylated piperidines, which are stated to liberate iodine from potassium iodide.

A close analogy may be traced between these oxamines and the alkylated oxyphosphines, oxyarsines, and oxystibines.

The method now described for the preparation of the examines is very easy to carry out and gives an excellent yield. It is on this account to be preferred to the process by which the authors prepared the first member of this series of compounds, namely, by the action of methylic iodide on hydroxylamine, inasmuch as this involves a troublesome separation of the examine from the salts of hydroxylamine which accompany it.

Action of Hydrogen Peroxide on Trimethylamine. Formation of Trimethyloxamine, (CH₂)₂N:O.

An aqueous solution of trimethylamine containing about 3 grams of the base was mixed with the calculated quantity of hydrogen peroxide (60 c.c. of a 3 per cent. solution, previously freed from sulphuric acid by shaking with barium carbonate) and the mixture was allowed to stand for 24 hours at the ordinary temperature. The ammoniacal smell of the trimethylamine gradually disappeared.

The solution was concentrated to a small volume (about 20 c.c.) by distillation under reduced pressure. On the addition of dilute hydro-

chloric acid in slight excess, some evolution of nitrous fumes occurred, indicating the presence of a nitrite. The acidified solution was evaporated on the water-bath until the volume was reduced to about 5 c.c. On cooling, a salt crystallised out which closely resembled the hydrochloride of trimethyloxamine. The crystals were removed, washed with ethylic alcohol, and recrystallised from hot methylic alcohol. On concentrating the mother liquor, more of the same salt was obtained and purified in the same manner. The whole of the purified material was then again recrystallised from hot methylic alcohol, washed with ethylic alcohol, drained on a porous tile, and dried in the water-oven. The properties of this salt were precisely those of the trimethyloxamine hydrochloride previously described by the authors.

0.2522 furnished 0.3228 AgCl. Cl = 31.7. (CH₂).NO,HCl requires Cl = 31.8 per cent.

The platinichloride was prepared and recrystallised from methylic alcohol. Its properties agreed with those of the trimethyloxamine salt.

0.1401 gave, on ignition, 0.0486 Pt. Pt = 34.6.

 $[(CH_3)_3NO]_2, H_2PtCl_6$ requires Pt = 34.8 per cent.

The aurichloride crystallised from hot water in yellow octahedra.

0.0995 of a recrystallised specimen gave 0.0471 Au. Au = 47.3. $(CH_g)_2NO_1HAuCl_4$ requires Au = 47.5 per cent.

The hydrated base, $(CH_3)_3N:O+2H_2O$, was prepared by the addition of moist silver oxide to a solution of the hydrochloride in just sufficient quantity to remove the whole of the chlorine. The solution was filtered and evaporated nearly to dryness on the water-bath. On cooling, the base crystallised rapidly in radiating needles in the manner characteristic of trimethyloxamine.

This substance was strongly alkaline to litmus, and possessed all the properties of trimethyloxamine, showing the same reactions with silver nitrate, cupric sulphate, and ferrous sulphate.

The action of hydrogen peroxide on an aqueous solution of trimethylamine constitutes the best method of preparing trimethyloxamine, which was first obtained by the authors by the action of hydroxylamine on methylic iodide.

Action of Hydrogen Peroxide on Triethylamine. Formation of Triethyloxamine, (C₂H₅)₈N:O.

Three grams of triethylamine were mixed with 34 c.c. of a 3 per cent. solution of hydrogen peroxide (these quantities being in approximately molecular proportion) and allowed to stand with occasional agitation

for 24 hours. The oily base completely disappeared. When the solution was evaporated on the water-bath, a thick, colourless liquid was obtained, which was strongly alkaline to litmus, and crystallised after remaining for several days in a vacuous desiccator. This substance exhibited all the reactions of the triethyloxamine obtained by the action of ethylic iodide on diethylhydroxylamine. It formed an applegreen precipitate with solution of cupric sulphate, which, on warming, subsided as a pale blue powder. With solution of silver nitrate, a white precipitate was produced, reduced to metallic silver on heating. When a solution of the base was added to solution of ferrous sulphate, it immediately became reddish-brown, and ferric hydroxide separated.

In a second experiment, the triethylamine was mixed with 6 per cent. solution of hydrogen peroxide. After shaking for a few minutes, the solution became quite warm, and the layer of triethylamine rapidly grew smaller and finally disappeared. On evaporating the solution, the triethyloxamine remained as a thick, colourless liquid.

In order to completely characterise the oxamine, the following salts were prepared:

The hydrochloride, (C₂H₅)₈NO,HCl, was obtained as a sticky liquid, which crystallised in the desiccator in deliquescent needles.

The platinichloride, [(C₂H₅)₈NO]₂,H₂PtCl₆, is very soluble in water and methylic alcohol, slightly soluble in cold ethylic alcohol, but more soluble in hot. After recrystallising twice from hot ethylic alcohol, the platinum was determined by ignition.

```
0.1231 gave 0.0372 Pt. Pt = 30.2.

0.0549 ,, 0.0167 Pt. Pt = 30.4.

[(C_2H_5)_8NO]_9H_2PtCl_6 requires Pt = 30.3 per cent.
```

The aurichloride, (C₂H₅)₃NO,HAuCl₄, separates as an oil when auric chloride is added to a solution of the hydrochloride. It is somewhat soluble in hot, but very sparingly soluble in cold water.

The picrate, $(C_2H_5)_3NO$, $C_6H_2(NO_2)_3OH$, is obtained as a pale yellow precipitate when a cold saturated solution of picric acid is added to an aqueous solution of triethyloxamine. This salt is soluble in hot water and crystallises on cooling in fine, yellow needles which soften above 160° and melt at 164° .

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0.3355 gave 0.5098 CO_2 and 0.1587 H_2O. C = 41.44; H = 5.26. (C_2H_5)_3NO, C_6H_2(NO_2)_3OH requires C = 41.62; H = 5.20 per cent.
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The following experiment was made in order to ascertain the extent to which the formation of triethyloxamine takes place.

One gram of triethylamine was mixed with 6 c.c. of 6 per cent. solution of hydrogen peroxide. After standing for about 24 hours, cold saturated aqueous picric acid solution was added in excess. The

precipitate was collected on a tared filter, dried, and weighed. 2.5 grams were thus obtained. It was found that triethyloxamine picrate is soluble to about the extent of 0.6 gram in 100 c.c. of water at the temperature at which the experiment was carried out; hence the filtrate (which measured 150 c.c.) contained about 0.9 gram of the picrate in solution. The total weight of picrate formed was therefore 3.4 grams, which is exactly that required by the equation $(C_2H_5)_3N+O=(C_2H_5)_3NO$, so it may be concluded that the reaction takes place quantitatively.

Action of Hydrogen Peroxide on Tripropylamine. Formation of Tripropyloxamine, (C₂H₇)₂N:O.

Owing chiefly to its insolubility, tripropylamine is scarcely at all attacked by an aqueous solution of hydrogen peroxide. If, however, the base is dissolved in alcohol, it can be readily oxidised and converted into its oxamine. The following plan has been found to answer best.

About 4 grams of tripropylamine are dissolved in 30 c.c. of ethylic alcohol, 16 c.c. of hydrogen peroxide (6 per cent.) are added, and the mixture is warmed for about 12 hours at 60°. The liquid is distilled under reduced pressure until about two-thirds have passed over. The syrupy residue, if placed in a vacuous desiccator, soon becomes very thick, and finally crystallises in radiating needles, which dissolve readily in water and alcohol, but are insoluble in ether.

As thus obtained, tripropyloxamine is a very hygroscopic substance which acts as a strong base; it is alkaline to litmus, and combines energetically with acids, forming well-defined salts. It has a bitter taste.

The hydrochloride, (C₈H₇)₈NO,HCl, may be obtained by adding hydrochloric acid to a solution of the base and evaporating to dryness. The gummy residue soon crystallises on standing. The salt is readily soluble in water, alcohol, and chloroform, but is insoluble in ether. It is best purified by precipitating it by the addition of ether to an alcoholic solution. When heated, it gradually softens, and is completely melted at about 90°.

The picrate, $(C_3H_7)_8NO$, $C_6H_2(NO_2)_8OH$, is a characteristic salt which is precipitated when an aqueous solution of picric acid is added to a solution of the base. It is remarkable in being nearly insoluble in cold water. Hot water dissolves it, and crystals separate on cooling which melt at 129°.

The platinichloride, [(C₃H₇)₈NO]₂, H₂PtCl₆, is nearly insoluble in cold water, but crystallises readily from hot water in orange-red

prisms melting at 174—175°. This salt, recrystallised from water, was analysed with the following result:

0.1377 gave 0.0368 Pt. Pt = 26.73. $[(C_3H_7)_3NO]_2, H_2PtCl_6 \text{ requires Pt} = 26.76 \text{ per cent.}$

The aurichloride, (C₃H₇)₃NO,HAuCl₄, is precipitated as an oil when auric chloride is added to a solution of the hydrochloride. From warm water, it crystallises in golden spangles. This salt is slightly soluble in cold water, rather more soluble in hot water, and readily dissolved by alcohol. On analysis, a specimen dried at 100° furnished the following result:

0.0871 gave 0.0342 Au. Au = 39.3. $(C_3H_7)_8NO, HAuCl_4$ requires Au = 39.5 per cent.

Tripropyloxamine exhibits generally the same properties and reactions as the trimethyl- and triethyl-oxamines already described. With copper sulphate, it furnishes a pale blue precipitate, with ferrous sulphate, it produces ferric hydroxide, undergoing reduction, whilst it readily reduces solution of silver nitrate. It does not liberate iodine from potassium iodide or show any other evidence of being a powerful oxidising agent.

Action of Hydrogen Peroxide on Dimethylamine.

Two grams of dimethylamine (in 33 per cent. aqueous solution) were mixed with 25 c.c. of hydrogen peroxide (6 per cent. solution). After standing for a short time, the solution became warm and smelt of formaldehyde; small quantities of oxygen were continuously evolved. After 24 hours all the hydrogen peroxide had disappeared, but it was found that only about half of the dimethylamine had been attacked. The chief products of oxidation appeared to be nitrous acid, formic acid, and formaldehyde. No β -dimethylhydroxylamine, corresponding to the products of the action of hydrogen peroxide on diethylamine and dipropylamine, could be detected. The solution contained a small quantity of a substance which, after boiling with dilute acid, reduced Fehling's solution in the cold, but it was present in too small amount to be identified.

Action of Hydrogen Peroxide on Diethylamine. Formation of β -Diethylhydroxylamine, $(C_2H_5)_2N$ -OH.

Diethylamine was dissolved in the calculated quantity of solution of hydrogen peroxide (6 per cent.) and the mixture allowed to stand at the ordinary temperature for 24 hours. The whole of the hydrogen peroxide had then disappeared, and the solution had become slightly

yellow, and had acquired the characteristic odour of β -diethylhydroxylamine, $(C_2H_5)_2N\cdot OH$. The liquid was shaken with ether, the ethereal solution dried with calcium chloride, and the ether carefully distilled off. The residue was a very basic liquid, having all the properties of β -diethylhydroxylamine, and giving the same reactions with solutions of cupric sulphate, silver nitrate, and mercuric chloride.

When an ethereal solution of anhydrous oxalic acid was added to an ethereal solution of the base, the *oxalate* of β -diethylhydroxylamine, $[(C_2H_5)_2N\cdot OH]_2H_2C_2O_4$, was precipitated, which, after recrystallisation, melted at 136—137°, and exhibited the crystalline form and properties characteristic of that salt, as described in a previous paper (*loc. cit.*). A determination of the oxalic acid gave the following result:

0.2143 of salt gave 0.0443 CaO.
$$H_2C_2O_4 = 33.2$$
. $[(C_2H_5)_2N\cdot OH]_{27}H_2C_2O_4$ requires $H_2C_2O_4 = 33.6$ per cent.

The yield of β -diethylhydroxylamine furnished by this reaction is probably not more than about 50 per cent. of that required by the equation $(C_2H_5)_2NH+O=(C_2H_5)_2N\cdot OH$.

Action of Hydrogen Peroxids on Dipropylamins. Formation of β -Dipropylhydroxylamins, $(C_8H_7)_2N\cdot OH$.

Dipropylamine was mixed with the calculated quantity of hydrogen peroxide (6 per cent.) and allowed to stand for 24 hours with occasional agitation. It was found that no hydrogen peroxide remained, and that a substance had been produced which reduced Fehling's solution in the cold and possessed the curious odour characteristic of β -dipropylhydroxylamine. The mixture was extracted with ether, and the ethereal solution dried with calcium chloride. The ether was distilled off and an oily residue remained.

To 1 gram of this residue a strong, warm, aqueous solution of 1 gram of oxalic acid was added. The solution was concentrated on the water-bath, and on cooling a salt crystallised out in rosettes of plates. The crystals were removed from the mother liquor, washed with a little cold water and alcohol, and recrystallised from warm alcohol. The recrystallised salt melted at 139°, was acid to litmus, and exhibited all the characters of the acid oxalate of β -dipropylhydroxylamine, $(C_3H_7)_2N\cdot OH, H_2C_2O_4$. A determination of the oxalic acid gave the following result:

```
0.3430 gave 0.0928 CaO. H_2C_2O_4 = 43.5. (C_3H_7)_2N\cdot OH, H_2C_2O_4 requires H_2C_2O_4 = 43.5 per cent.
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The free base exhibited the reactions with cupric sulphate, mercuric

chloride, and silver nitrate which have been described for β -dipropylhydroxylamine in the authors' previous paper (loc. cit.).

The yield was only about 50 per cent. of that required by the equation $(C_3H_7)_2NH+O=(C_3H_7)_2N\cdot OH$.

In conclusion, we may remark that we have tried a number of experiments on the action of hydrogen peroxide, under different conditions, on ammonia and its salts, in the hope of effecting the production of hydroxylamine. All these experiments have, however, been unsuccessful. It has not been possible in any case to detect the presence of hydroxylamine in the product.

With regard to the possibility of producing monosubstituted hydroxylamines by the oxidation of primary amines, all experiments have been unsuccessful, the primary amine being completely decomposed, forming nitrous acid among other products. It has been observed also that primary amines are not rapidly attacked by hydrogen peroxide at the ordinary temperature. Experiments have also been made with numerous other amines and amino-derivatives, as a rule with little or no result. Ethylenediamine, however, is vigorously decomposed by hydrogen peroxide, and the products of the change are now under investigation.

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XCVIII.—Amidoamidines of the Nuphthalene Series.

By RAPHAEL MELDOLA, F.R.S., and PERCY PHILLIPS.

ETHENYLTRIAMIDONAPHTHALENE was made known by one of the authors and F. W. Streatfeild in 1887 (Trans., 51, 691) as a representative of the amidoamidines of the naphthalene series. Various salts and derivatives of the base were described in the paper referred to, and the diazotisable character of the amido-group was indicated by the formation of the azo-derivative of β -naphthol. The investigation of the compound has been carried on at intervals since the time of its discovery, but it has not been considered that sufficient material had been obtained to warrant further publication. Among other properties of the base which have received special attention are its power of combining with diazotised amido-compounds of various kinds and the introduction of acid radicles into the amido-group. With respect to the secondary disazo-derivatives of the anhydro-base, we may point out that these appear to have a special affinity for vegetable

fibre, and they have accordingly been made the subject of a German patent (Farbwerk Friedrichsfeld, Dr. Paul Remy, Germ. Pat. 98141 of 1897). The cost of the original anhydro-base is, however, too great to hold out much hope of these colouring matters becoming of technical importance.

With regard to the acetyl derivative of the base, it was stated in the original paper (loc. cit., p. 698) that no definite result had been arrived at. It was found, however, soon after the publication of that paper, that the method of acetylation employed originally, namely, boiling with acetic anhydride and sodium acetate, was much too violent, and led to great loss of material through the formation of resin. It was for this reason that we failed to isolate the acetyl derivative, working as we did on a small scale. In the meantime, another investigator (Markfeldt, Ber., 1898, 31, 1174)* has entered the field, and by working on a larger scale has succeeded in preparing the acetyl derivative. Unfortunately, Markfeldt does not state the yield of the latter compound obtained by his method, but his description of the process of purification leaves no doubt that his product was largely contaminated with resin. We have convinced ourselves, moreover, by experiment, that Markfeldt's method of boiling for some hours with the acetic anhydride and sodium acetate is not only unnecessary, but absolutely destructive. We find that even boiling with acetic acid and acetic anhydride for one hour gives a product containing much resin.

The process, which in our hands has been found to give the acetyl derivative in practically quantitative yield and with no admixture of resin, is as follows: The dry salt of the anhydro-base (preferably the sulphate) is ground up in a mortar with glacial acetic acid, acetic anhydride, and dry sodium acetate. The acetylation takes place at the ordinary temperature, and may be completed, if necessary, by warming on a water-bath for a few minutes. The product is diluted with water, allowed to stand till the excess of acetic anhydride is decomposed, and then exactly neutralised with ammonia. The acetyl derivative separates as a crystalline pulp of white needles, and can be best purified by crystallisation from boiling water containing a little ammonia or very dilute caustic soda, the excess of alkali being

^{*} This author uses iron as the reducing agent in preference to tin, and claims as an advantage that the use of this metal dispenses with the troublesome removal of tin by sulphuretted hydrogen. It is, however, expressly stated in the original paper that "when the sulphate was required, it was found that the insolubility of this salt enabled us to separate it completely from the solution directly after reduction, without the previous removal of the tin, the latter being washed out by frequently treating the mass of crystals on the filter with water" (loc. cic., p. 692). We still find that this is by far the simpler method.



neutralised (after filtering off any insoluble matter) by dilute acid of any kind. If the free base is required, it is better to leave the solution slightly ammoniacal.

4-Acetamido-ethenyl-1: 2-naphthylenediamine.

The general characters of this compound have been described by Markfeldt, and since in most respects we can confirm his statements, it is unnecessary to repeat them. The melting point of our preparation was 280—282° with decomposition, but the substance begins to shrink and darken long before this temperature is reached, and the precise temperature of decomposition is very difficult to determine. The temperature at which shrinkage begins varies within a wide range according to the physical (crystalline) condition of the compound and the rate at which the bath is heated. The anhydrous acetyl derivative begins to shrink at 165° and decomposes at about 274°.

Some of the salts of the acetyl derivative are mentioned by Markfeldt, but neither analyses nor formulæ are given. The salts described are those resulting from the basic character of the compound. It was, however, pointed out in the original paper on ethenyltriamidonaphthalene (loc. cit., p. 699) that the NH-group of the amidine ring also possesses acid characters, and a silver compound was described which was obtained by precipitating an ammoniacal solution of the amidine with ammoniacal silver nitrate. The silver in this compound no doubt replaces the hydrogen of the NH-group. We may point out that the acid character of the NH-group in amidines has since been confirmed by other investigators (Bamberger and Lorenzen, Annalen, 1893, 273, 281) in the case of ethenyltoluylenediamine. The silver compounds obtained from the naphthylene anhydro-base and its acetyl derivative are gelatinous and incapable of being crystallised, so that purification for the purpose of analysis was not possible, and only approximate numbers could be obtained. The silver salt of the acetyl derivative is best prepared by dissolving the latter in alcohol with the addition of ammonia and adding to the warm solution an ammoniacal solution of silver nitrate diluted with alcohol as long as a precipitate forms. The silver salt is precipitated as a white, gelatinous substance which becomes more coherent on standing. After being collected and washed with alcohol containing a little ammonia, the compound dries to a whitish, amorphous mass which darkens under the influence of light. Specimens prepared in this way were found on analysis to contain 29.37 and 29.66 per cent. of silver and 12.4 per cent. of nitrogen, instead of the calculated amounts of 31.21 of silver and 12.14 of nitrogen. The low percentage of silver is probably due to partial dissociation of the salt on washing, but

the results are sufficient to indicate that the compound has the formula

$$C_2H_8O \cdot NH \cdot C_{10}H_5 \stackrel{NAg}{<} C \cdot CH_8.$$

In confirmation of this, it has been found possible to obtain alkyl derivatives by heating the silver salt with alkyl iodides, &c., in appropriate solvents.

The methyl derivative, $C_2H_3O \cdot NH \cdot C_{10}H_8 < N(CH_3) > C \cdot CH_8 + H_2O$, was prepared by boiling the silver salt, suspended in methylic alcohol, with methylic iodide for some hours. The alcoholic solution, after filtration, was evaporated to dryness, and the residue crystallised from boiling water with the addition of animal charcoal. It forms flat, silvery needles, which begin to darken and shrink at 200° and melt with decomposition and partial sublimation at about 250°.

The suppression of the acid character of the molecule by the replacement of the hydrogen of the NH-group by methyl produces a marked change in the properties of the compound. The original acetyl derivative is both acid and basic. It dissolves readily, especially when freshly precipitated and in a fine state of division, both in aqueous potassium and sodium hydroxides, and in aqueous ammonia; it dissolves also in dilute acids, and a very characteristic property is its behaviour with dilute hydrochloric acid, in which the acetyl derivative first dissolves, and then white, needle-shaped crystals of the hydrochloride begin to separate out. The methyl derivative, on the other hand, shows only basic properties. It is insoluble in alkalis and readily soluble in dilute acids; the hydrochloride is not deposited from its solution on standing. Analysis of a specimen, crystallised several times from dilute alcohol, gave the following result:

0.1062 gave 0.2594 CO₂ and 0.0630 H₂O. C = 66.61; H = 6.59. 0.0488 , 6.5 c.c. moist nitrogen at 15° and 759.2 mm. N = 15.57. $C_{15}H_{15}N_3O + H_2O$ requires C = 66.42; H = 6.27; N = 15.44 per cent.

The above (hydrated) specimen began to shrink at 200°, and fused with decomposition at 218°. The base tends to retain varying proportions of water, which cannot be driven off at 150° without the substance undergoing decomposition. The salts formed with mineral acids are very soluble, and we have not been able to isolate any one of them in a definite form. The solution of the hydrochloride gives no definite salt with platinic chloride.

The picrate is formed readily on mixing hot, alcoholic solutions of the base and picric acid. It is but slightly soluble in cold alcohol and consists of very slender, canary-yellow, silky needles, which begin to darken at 185°, and decompose with charring at 240—255°.

0.0606 gave 9 c.c. moist nitrogen at 15° and 762.6 mm. N = 17.43. $C_{15}H_{15}N_3O, C_6H_2(NO_2)_3.0H$ requires N = 17.43 per cent.

$$\begin{array}{c} \text{4-Benzamido-ethenyl-1: 2-naphthylenediamine,} \\ \text{C}_7\text{H}_5\text{O}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_5 \overset{\mathbf{NH}}{\sim} \text{C}\cdot\text{CH}_8. \end{array}$$

The benzoyl derivative of the anhydro-base is prepared by grinding the dry sulphate with dry sodium benzoate and enough benzoyl chloride to form a paste. The benzoylation is completed by heating for a short time on a water-bath, and the product isolated by washing with water and dilute alkali. The benzoyl derivative, like the acetyl derivative, is both acid and basic. It dissolves readily in alcoholic sodium hydroxide, and, when freshly precipitated, in aqueous ammonia. When crystallised from dilute alcohol, it consists of small ochreous scales which darken at 275° and decompose at 279—280°.

0.1892 gave 0.5091 CO₂ and 0.0948 H₂O. C=73.39; H=5.57.

This analysis agrees with that of the compound crystallised with $\frac{1}{2}H_2O$, as $C_{19}H_{15}N_3O + \frac{1}{2}H_2O$ requires C = 73.54; H = 5.16 per cent.

There is, however, reason to believe that this compound is capable of combining with varying quantities of water, as the numerous analyses of various preparations purified in different ways point to variations from the anhydrous substance to compounds with $\frac{1}{2}H_2O$ or $1H_2O$. Thus, a specimen obtained by basifying the hydrochloride gave the following results:

0·1526 gave 0·4205 CO₂ and 0·0725 H_2O . C = 75·15; H = 5·28. 0·1083 ,, 12·72 c.c. moist nitrogen at 13·4° and 762 mm. N = 13·85. $C_{19}H_{15}N_3O$ requires C = 75·74; H = 4·98; N = 13·95 per cent.

The free base is soluble in alcohol with some difficulty, and practically insoluble in ethylic acetate, chloroform, benzene, or toluene. It cannot be readily obtained in a crystalline condition, and is by no means a well characterised compound, being difficult to purify on account of its insolubility. Of the salts, the following have been prepared:

The hydrochloride, obtained by dissolving the base in alcoholic hydrochloric acid and dilution with water, forms small, white needles.

0.0743 gave 7.75 c.c. moist nitrogen at 9.5° and 752 mm. N = 12.37. 0.2381 , 0.1039 AgCl. Cl = 10.80.

 $C_{19}H_{15}N_8O$, HCl requires N = 12.44; Cl = 10.82 per cent.

The sulphate, prepared in a similar way, crystallises in small, whitish scales.

0.0796 gave 7.8 c.c. moist nitrogen at 10.25° and 755.8 mm. N = 11.66. 0.1028 gave 0.0354 BaSO₄. S = 4.72.

$$(C_{19}H_{15}N_8O)_2, H_2SO_4$$
 requires $N = 12.0$; $S = 4.57$ per cent.

The picrate is prepared by mixing alcoholic solutions of the base and picric acid, boiling, and allowing to crystallise. It is purified by crystallisation from alcohol, and forms small, golden-yellow scales, which begin to change at 210°, fuse at 231°, and decompose at 237°.

0.0914 gave 12.25 c.c. moist nitrogen at 16.5° and 759 mm. N = 15.53. $C_{19}H_{16}N_8O, C_6H_2(NO_2)_8\cdot OH$ requires N = 15.84 per cent.

Azo-derivatives of the Amidoamidine.

The diazotisable character of the amido-group has already been referred to. In order to ascertain whether the diazo-salts had the usual characters of such compounds, a specimen of iodo-ethenyl-naphthylenediamine was prepared by the replacement of the diazonium group by iodine. This iodo-derivative is both acid and basic in its properties. It dissolves in dilute alkaline solutions, from which it is precipitated by acids. It dissolves readily in dilute alcohol, and was purified for analysis by crystallisation from this solvent, and finally from ethylic acetate, from which it separates in the form of whitish nodules which begin to darken at 243°, and finally melt with decomposition at 248°.

0.1842 gave 14.5 c.c. moist nitrogen at 11.75° and 744 mm. N = 9.19. 0.1328 , 0.1018 gram AgI. I = 41.42.

$$C_{10}H_5I \stackrel{NH}{\sim} C \cdot CH_8$$
 requires $I = 41 \cdot 23$; $N = 9 \cdot 09$ per cent.

The NH₂-group of the anhydro-base is not only diazotisable, but the base itself readily combines with other diazotised bases. The products of the action of diazotised aniline and of the nitranilines have been prepared and studied, but these compounds have not the simple formulæ of amidoazo-compounds, such as might have been expected from their mode of formation. The percentage of nitrogen in every case is lower than that required by the formula of the amidoazo-compound. It is not improbable that the azo-group enters one of the ortho-positions, 3 or 5, forming a closed complex containing quinque-valent nitrogen in combination with hydroxyl or an acid radicle.

As the determination of the constitution of these compounds will involve much more experimental work, we desire now simply to describe the properties of a typical member, namely, that produced by the action of diazotised aniline on the amidoamidine. The compound in question separates as a dark violet, gelatinous precipitate on mixing

solutions of benzenediazonium chloride and the acetate of the anhydrobase in presence of sodium acetate. The product, after being basified by dilute ammonia, washed with water, and finally with alcohol and dried, crystallises from fusel oil in dull, bronzy scales melting and decomposing at 257—260°. It is but very sparingly soluble in ethylic alcohol, but more readily in boiling fusel oil; the solutions are dull red. It dissolves readily in alcoholic soda with an orange colour, but the alkali appears to resolve the compound into new products which are now under investigation. Aqueous alkali also appears to decompose the compound. Analyses of specimens repeatedly crystallised from fusel oil gave percentages of nitrogen ranging between 21.53 and 21.98, whereas the expected amidoazo-compound,

$$\mathbf{C_6H_5 \cdot N_2 \cdot C_{10}H_4(NH_3)} \!\! < \!\!\! \underbrace{\phantom{\mathbf{NH} \times \mathbf{NH} $

requires N = 23.25 per cent. Further crystallisation from a mixture of aniline and toluene did not alter the composition.

The investigation of these products will be continued with Mr. Lewis Eynon, who has given material assistance in the present research.

FINSBURY TECHNICAL COLLEGE.

XCIX.—Condensations of Anhydracetonebenzil and its Analogues with Aldehydes.

By Francis R. Japp, F.R.S., and Alexander Findlay, M.A., B.Sc. Japp and Owens (Trans., 1885, 47, 90) described two compounds which they believed had been formed by the condensation of benzil with ethylic alcohol under the influence of caustic potash: $C_{80}H_{24}O_4$ (m. p. 200—201°) and $C_{46}H_{34}O_4$ (m. p. 232°).

It was shown later by one of us (Trans., 1897, '71, 297) that the former compound was in reality anhydracetonedibenzil, $C_{31}H_{24}O_4$ (m. p. 194—195°), and that its formation in Japp and Owens's experiments was due to the presence of acetone in the "methylated spirit" (alcohol "denatured" with 10 per cent. of crude wood spirit) which was used instead of duty-paid alcohol in its preparation. No explanation was offered of the formation of the second compound.

The very complicated formula $C_{46}H_{34}O_4$ was adopted owing to the supposed necessity of explaining the formation of this compound from benzil and ethylic alcohol. If, however, it is in reality formed from benzil and acetone, it might have the formula $C_{24}H_{18}O_2$, which would agree equally well with the results of analysis. It is only necessary

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to assume that anhydracetonebenzil (diphenylcyclopentenolone), $C_6H_5 \cdot C \longrightarrow CH \longrightarrow CO$, is first formed; that another portion of the $C_6H_5 \cdot C(OH) \cdot CH_2 \longrightarrow CO$, is first formed; that another portion of the benzil is hydrolysed by the caustic potash in the usual way to benzaldehyde and benzoic acid; and that the benzaldehyde then interacts with the anhydracetonebenzil, yielding benzylideneanhydracetonebenzil, $C_6H_5 \cdot C \longrightarrow CH \longrightarrow CO$

This supposition proved to be correct. A mixture of anhydracetonebenzil and benzaldehyde, allowed to stand with dilute alcoholic caustic potash in the cold, gave an excellent yield of a compound indistinguishable from that prepared by Japp and Owens, with whose original specimen we compared it.

As all attempts to prove directly the presence of the hydroxyl group in anhydracetonebenzil had hitherto failed, on account of the ease with which the compound splits off water under the influence of acetic anhydride, we tried to acetylate this benzylidene derivative, but found that acetic anhydride was without action on it even in a sealed tube at 150°. Addition of potassium acetate or of zinc chloride to the mixture did not bring about the reaction.

Boiling for a short time with fuming hydriodic acid reduces benzylideneanhydracetonebenzil to a compound of the formula C₂₄H₁₈O (m. p. 182°), which is probably a benzylidenediphenylcyclopentenone—either

The change in the position of the double bonds in the latter formula would correspond with the migration which occurs in the reduction of anhydracetonebenzil to diphenylcyclopentenone. An attempt was made to obtain this compound directly by the condensation of diphenyl-

cyclopentenone, C_6H_5 , $C \cdot CH_2$ CO (Trans., 1897, 71, 123), with benzaldehyde under the influence of alcoholic caustic potash. The condensation readily took place; but the product appeared to be a mixture, and the small quantity at our disposal did not suffice for purification.

By the condensation of anhydracetonebenzil with cuminaldehyde, we prepared cumylideneanhydracetonebenzil,

$$\begin{array}{c} C_6H_5\cdot C \longrightarrow CH > CO \\ C_6H_5\cdot C(OH)\cdot C \longrightarrow CH\cdot C_6H_4\cdot C_3H_7 \end{array}$$

(m. p. 148°), and with cinnamaldehyde, cinnamylideneanhydracetonebensil, $C_6H_5 \cdot C \longrightarrow CH \rightarrow CO$ $C_6H_5 \cdot C(OH) \cdot C \longrightarrow CH \cdot CH \cdot CH \cdot C_6H_5$ (m. p. 220°).

These condensation compounds of anhydracetonebenzil with alde-

hydes have an intense yellow colour. In all probability, the yellow colour of crude anhydracetonebenzil, from which the compound cannot be freed except by partial oxidation, is due to the presence of a small quantity of the benzylidene derivative.

Condensation with aldehydes has of late years been employed by Wallach and others to determine the constitution of cyclic ketones, the condensation taking place only when the ketone contains a methylene group directly attached to carbonyl. It occurred to us that this reaction might be employed to decide the constitution of the monalkyl homologues and other mono-substitution derivatives of anhydracetonebenzil, in which the substituent may replace hydrogen either of the CH-group or of the CH₂-group in anhydracetonebenzil. We will distinguish these two classes as α- and β-derivatives respectively: *

$$\begin{array}{c} C_6H_5 \cdot C \longrightarrow CR' \\ C_6H_5 \cdot C(OH) \cdot CH_2 \\ \text{a.Derivative.} \end{array} > CO. \qquad \begin{array}{c} C_6H_5 \cdot C \longrightarrow CH \\ C_6H_5 \cdot C(OH) \cdot CHR' \\ \end{array} > CO.$$

We anticipated that the condensation with an aldehyde would take place only in the case of a-derivatives.

Japp and Lander (Trans., 1897, 71, 129) distinguished between these two classes of derivatives by means of the rate at which the substances decolorised permanganate, as only those ethylene derivatives in which hydrogen is directly attached to the unsaturated carbon atoms are rapidly oxidised by this agent. In this way they arrived at the conclusion that the known monalkyl derivatives of anhydracetonebenzil belonged to the β -series. In accordance with this view, we found that amylanhydracetonebenzil (m. p. 150.5°), which we selected for experiment, did not yield a benzylidene derivative.

* This nomenclature has already been employed in the case of the two anhydrobenzils wulic (anhydracetonebenzilethyloic) acids (Trans., 1897, 71, 145).

+ Since the publication of the preliminary note on this subject (Proc., 1899, 15, 164) I have, along with Mr. A. N. Meldrum, made some observations which show that the condensation with aldehydes cannot always be depended upon to distinguish between the α- and β-mono-substitution derivatives of anhydracetonebenzil. By the condensation of methyl ethyl ketone with benzil we have obtained, in addition to the methylanhydracetonebenzil melting at 179° prepared by Japp and Burton, an isomeride melting at 118°. The former compound is rapidly attacked by permanganate, the latter only slowly; and the two compounds should therefore have the formulæ

$$C_6H_5 \cdot C = C(CH_8) \sim CO$$
 and $C_6H_5 \cdot C = CH \sim CO$.

 $C_6H_5 \cdot C(OH) \cdot CH_9 \sim CO$.

 $C_6H_5 \cdot C(OH) \cdot CH(CH_8) \sim CO$.

 $C_6H_5 \cdot C = CH \sim CO$.

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In accordance with this constitution, the a-compound readily yields a benzylidene

Japp and Murray (Trans., 1897, 71, 145) assigned to a-anhydrobenzillævulic acid the constitution of an a-anhydracetonebenzilethyloic acid, ${}^{C_6H_5} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {}^{C} \cdot {$

$$\begin{array}{c|c} C_6H_5 \cdot C & -CH_2 \cdot COOH \\ > CO \\ C_6H_5 \cdot C(OH) \cdot C - CH \cdot C_6H_5 \end{array}$$

(m. p. 214-216°).

Japp and Lander (Trans., 1897, 71, 139) found that anhydracetonebenzilcarboxylic acid, $C_6H_5 \cdot C = CH > CO$ benzilcarboxylic acid, $C_6H_5 \cdot C(OH) \cdot CH = COOH$, is rapidly oxidised by permanganate in the cold, whilst isophenanthroxyleneacetoacetic acid, C₆H₄·C COOH, is not oxidised. This indicates that the former is a β -, the latter an α -carboxy-compound, as here formulated. The results of the benzaldehyde condensation would, however, lead to exactly the opposite conclusion, inasmuch as the former compound yields a benzylidene derivative, whilst the latter does not. We incline, however, to accept the evidence of the permanganate reactions, as the discrepant results obtained by the other method readily admit of explanation. Thus in the formation of benzylideneanhydracetonebenzilcarboxylic acid, it was found necessary to allow the interacting substances to stand in the cold for five weeks, and even then a quantity of anhydracetonebenzilcarboxylic acid was recovered unchanged. There was, therefore, ample opportunity for a portion of the anhydracetonebenzil-β-carboxylic acid to be transformed into the α-compound, which would then interact with the benzaldehyde to form benzylidene-

derivative, the condensation being complete in the cold in 24 hours. But the β -compound also interacts with benzaldehyde, yielding the same benzylidene derivative as the a-compound, the process, however, taking place so slowly, that, even after allowing the mixture of β -compound, benzaldehyde, and alcoholic caustic potash to stand for a month, only a small quantity of benzylidene derivative is formed, whilst a further part of the β -compound yields an aldol condensation compound with the benzaldehyde, and part remains unchanged. It must be left for future investigation to clear up the precise order in which these reactions occur; but it is evident from the foregoing that, under these conditions, β -methylanhydracetonebenzil is, in course of time, converted into an α -derivative, and that therefore, where the action is slow, the condensation with aldehydes cannot be safely employed in determining the constitution of compounds of this class. In such cases, the behaviour of the compounds towards permanganate probably furnishes a more trustworthy criterion. This applies to the case of anhydracetonebenzilearboxylic acid, discussed in the present paper.—F. R. J.

(m. p. about 245°, with decomposition), the process being thus analogous to the formation of benzylidene-α-methylanhydracetonebenzil from β-methylanhydracetonebenzil, already referred to.* As regards the fact that isophenanthroxyleneacetoacetic acid, although both from its mode of formation and from its stability towards permanganate it must be regarded as an α-compound, does not yield a benzylidene derivative, this is amply accounted for by the insolubility of its potassium salt in alcohol, whereby the substance is at once withdrawn from action.

It is evident from the foregoing that the applicability of the condensation with benzaldehyde to determining the constitution of monosubstitution derivatives of anhydracetonebenzil is very restricted. If the condensation takes place rapidly and completely, we may assume that we are dealing with an α -compound. But it would be dangerous to deduce the presence of an α -compound from a slow and imperfect condensation, or of a β -compound from the non-occurrence of the condensation.

Anhydracetonebenzil and benzil interact in presence of alcoholic caustic potash to form an aldol condensation compound,

$$\begin{array}{c} C_6H_5 \cdot C = = CH \\ C_6H_5 \cdot C(OH) \cdot CH \\ C_6H_5 \cdot CO \cdot C(OH) \cdot C_6H_5 \end{array},$$

identical with anhydracetonedibenzil, previously obtained by the condensation of acetone with excess of benzil (Trans., 1885, 47, 33). The hitherto unknown constitution of anhydracetonedibenzil is thus ascertained.

By the reduction of anhydracetonedibenzil with hydriodic acid Japp and Lander obtained two isomeric products—small prisms melting at 187—188°, and pyramids melting at 155—159°—to which, in their first communication on the subject (Proc., 1895, 11, 147), they assigned the formula $C_{31}H_{24}O$. The compound melting at 187—188° was also obtained in the reduction of ethylic anhydrodibenzilaceto-acetate. In a later communication (Trans., 1896, 69, 744—746), they changed the formulæ of these compounds to $C_{28}H_{22}O$, with which the results of analysis also agreed.† This, however, would mean that the

^{*} At the time of writing the preliminary note already referred to, this reaction of β -methylanhydracetonebenzil had not been observed, so that we were unaware of the possibility of this intramolecular change, and consequently altered (as we now consider, unnecessarily) the formula given by Japp and Lander for anhydracetone-benzilcarboxylic acid from the β - to the α -form.

[†] The change was made in order to account for the behaviour of one of the derivatives of ethylic anhydracetonedibenzilacetoacetate on reduction.

three atoms of carbon derived from acetone had been removed during the reduction, leaving the two benzil complexes united together—a supposition which cannot be brought into harmony with the foregoing constitution of anhydracetonedibenzil. The composition of the two isomeric reduction compounds must therefore be represented by the formula $C_{81}H_{24}O$, the reactions occurring according to the equation

$$C_{81}H_{24}O_4 + 3H_2 = C_{81}H_{24}O + 3H_2O.$$
Anhydraetone-dibensil

The homologues of acetone do not yield condensation compounds with 2 molecules of benzil, so that the homologues of anhydrace-tonedibenzil are unknown. An attempt to prepare one of these by the condensation of amylanhydracetonebenzil with benzil gave no result. Amylanhydracetonebenzil does not condense with benzil any more than with benzaldehyde.*

We had hoped to obtain an open-chain benzylidene derivative from $C_6H_5 \cdot C(OH) \cdot CH_2 \cdot CO \cdot CH_8$ acetonebenzil, $C_6H_5 \cdot CO$, and benzaldehyde; but only benzylideneanhydracetonebenzil was formed. This failure was doubtless due to the ease with which acetonebenzil in presence of caustic potash parts with water, forming the closed-chain compound, anhydracetonebenzil.

An open-chain compound of the desired character was, however, obtained by the condensation of benzylideneacetone with benzil:

This compound may receive the name desylenebenzylideneactors. It melts at 200°. The ease with which it changes into the isomeric benzylideneanhydracetonebenzil (m. p. 230°) prevented its specific reactions from being studied. This change, which takes place when the compound is heated, or when it is acted on either by ammonia or by hydrochloric acid, may be represented as follows:

This mode of formation of benzylideneanhydracetonebenzil may be regarded as a further proof that anhydracetonebenzil has the constitution of a diphenylcyclopentenolone.

^{*} It is, of course, quite possible that the newly-discovered a-monalkyl derivatives may interact with benzil.

When reduced with hydriodic acid, desylenebenzylideneacetone yields a compound, $C_{24}H_{18}O$ (m. p. 182°), identical with the product of the reduction of benzylideneanhydracetonebenzil (vide supra). Thus, none of the characteristic transformations into lactones, lactams, furfurans, and chlorofurfurans which unsaturated γ -diketones undergo under the foregoing conditions (compare Japp and Klingemann, Trans., 1890, 57, 662) are exhibited by this compound.

EXPERIMENTAL.

Anhydracetonebenzil and Benzaldehyde.—A mixture of 5 grams of anhydracetonebenzil, 2.5 grams of benzaldehyde, and 60 c.c. of absolute alcohol in which 0.25 gram of caustic potash had previously been dissolved, was allowed to stand in a corked flask for a fortnight, shaking it from time to time. The solid was separated by filtration, washed with cold alcohol to remove alkali, boiled with a little hot alcohol to remove unaltered anhydracetonebenzil, filtered off, and washed with hot alcohol. It weighed 5.4 grams. It was dissolved in a large bulk of boiling alcohol, from which, on cooling, it crystallised in bright yellow, microscopic, six-sided laminæ, melting constantly at 230° (232° Japp and Owens). It is very sparingly soluble, even in boiling alcohol.

0.1389 gave 0.4339 CO_2 and 0.0686 H_2O . C=85.19; H=5.48. $C_{24}H_{18}O_2$ requires C=85.20; H=5.32 per cent.

The compound is therefore benzylideneanhydracetonebenzil,

$$C_6H_5 \cdot C = CH > CO$$

 $C_6H_5 \cdot C(OH) \cdot C = CH \cdot C_6H_5$.

It is not acted on by acetic anhydride.

By boiling it for 5 minutes with fuming hydriodic acid, it was reduced to a compound which, after freeing it from iodine by means of sulphurous acid and recrystallising it from alcohol, formed faintly yellow needles melting at 182° . Analysis gave figures pointing to the formula $C_{24}H_{18}O$.

0.1489 gave 0.4861 CO₂ and 0.0793 H₂O.
$$C = 89.03$$
; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C = 89.41$; $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires $C_{24}H_{18}O$ requires C_{2

It is probably a benzylidenediphenylcyclopentenone (see introduction). An attempt to carry the reduction further by heating benzylidene-anhydracetonebenzil with hydriodic acid and amorphous phosphorus in a sealed tube at 150° yielded only an uncrystallisable resin.

Anhydracetonebenzil and Cuminaldehyde.—5 grams of anhydracetonebenzil, 3 grams of cuminaldehyde, 0.25 gram of caustic potash, and 60 c.c. of absolute alcohol were taken, and the mixture was allowed to stand for 10 days. Everything passed into solution. Water was

then added; the precipitated substance was taken up with ether, and the ethereal solution was shaken, first with hydrogen sodium sulphite, and then with sodium carbonate, evaporated to a small bulk, and light petroleum added to it. The crystalline substance which separated was recrystallised from benzene, from which it was deposited in slender, yellow needles melting at 148°. Analysis gave figures agreeing with the formula of cumylideneanhydracetonsbenzil, $C_6H_5 \cdot C \longrightarrow CH \rightarrow CO$ $C_6H_5 \cdot C \rightarrow CH \rightarrow CO$ $C_6H_5 \cdot C \rightarrow CH \cdot C_6H_4 \cdot C_8H_7$.

The ready solubility of this substance admitted of the cryoscopic determination of its molecular weight. The following figures were obtained, using glacial acetic acid as a solvent:

Wt. substance. Wt. solvent. Depression. Mol. wt.
$$0.1531$$
 20.22 0.08° 367 $C_{27}H_{24}O_2 \doteq 380$.

Anhydracetonebenzil and Cinnamaldehyde.—5 grams of anhydracetonebenzil, 3 grams of cinnamaldehyde, 0.25 gram of caustic potash, and 60 c.c. of absolute alcohol were taken, and the mixture was allowed to stand for 6 days. The purification of the product was effected exactly as in the case of the benzylidene derivative, except that the substance was finally recrystallised from glacial acetic acid, because the crystals from alcohol left an ash on combustion. The substance, thus purified, was free from mineral matter, and formed yellow, feathery crystals melting at 222°. It is sparingly soluble both in alcohol and in acetic acid. Analysis gave figures agreeing with the formula of cinnamylideneanhydracetonebenzil,

$$C_6H_5 \cdot C = CH > CO$$

 $C_6H_5 \cdot C(OH) \cdot C = CH \cdot CH \cdot CH \cdot C_6H_5$.

0.1847 gave 0.5784 CO_2 and 0.0942 H_2O . C = 85.41; H = 5.66. $C_{26}H_{20}O_2$ requires C = 85.71; H = 5.49 per cent.

a-Anhydrobenzillævulic Acid and Benzaldehyde.—5 grams of a-anhydrobenzillævulic acid were dissolved in absolute alcohol; the equivalent quantity of caustic potash, dissolved in alcohol, was added, so as to form the potassium salt; then 2 grams of benzaldehyde, and finally 0.25 gram of caustic potash, dissolved in alcohol so as to bring the entire bulk of liquid up to 70—80 c.c. Owing to the sparing solubility of the potassium salt, the mixture was allowed to stand for over seven months, shaking it from time to time. The precipitate was

filtered off, washed with alcohol, dissolved in water, and the solution acidified with dilute sulphuric acid. The precipitated organic acid was purified by recrystallisation from a mixture of ethylic acetate and light petroleum. It was deposited in two forms: small warts of white needles, and separate clear needles; but on standing under the solution the latter disappeared, being apparently converted into the former, so that the difference was probably due to dimorphism. It melted at 214—216°, evolving gas. Analysis agreed with the formula of benzyl-

$$\begin{array}{c|c} C_6H_5 \cdot C \longrightarrow C - CH_2 \cdot COOH \\ \hline ilono-a-anhydrobenzillavulic acid, & C_6H_5 \cdot C(OH) \cdot C \longrightarrow CH \cdot C_6H_5 \\ \hline \\ C_6H_5 \cdot C(OH) \cdot C \longrightarrow CH \cdot C_6H_5 \\ \hline \end{array}$$

0.1850 gave 0.5326 CO₂ and 0.0875 H₂O. C = 78.52; H = 5.25. $C_{26}H_{20}O_4$ requires C = 78.79; H = 5.05 per cent.

Neither the silver salt nor the barium salt could be obtained pure. Anhydracetonebenzil-β-carboxylic Acid and Benzaldehyde.—5 grams of anhydracetonebenzil-β-carboxylic acid, 1·25 grams of caustic potash, 2 grams of benzaldehyde, and 60 c.c. of absolute alcohol were employed, and the mixture was allowed to stand, with frequent shaking, for five weeks. The product was treated as in the preceding reaction. The liberated acid was purified by recrystallisation, first from dilute, afterwards from glacial, acetic acid. It formed yellow needles which melted, with darkening and evolution of gas, at about 245°. Analysis gave figures agreeing with those required for benzylideneanhydracetonebenzil-a-carboxylic acid,

$$\begin{array}{c|c} C_0H_5 \cdot C & C - COOH \\ & > CO \\ C_0H_5 \cdot C(OH) \cdot C - CH \cdot C_0H_5 \end{array}.$$

A quantity of anhydracetonebenzil- β -carboxylic acid was recovered unchanged.

Anhydracetonebenzil and Benzil.—6 grams of anhydracetonebenzil, 5 grams of benzil, 0.25 gram of caustic potash, and 60 c.c. of absolute alcohol were employed, and the mixture was allowed to stand for a fortnight, shaking it from time to time. The solid portion was filtered off, washed with ether, and dissolved in hot benzene. It separated in needles, which, if allowed to stand under the mother liquor, were gradually transformed into large, lustrous, tabular crystals—a behaviour characteristic of anhydracetonedibenzil. The

^{*} The reasons for assuming a change from the β - to the α -modification in the formation of this compound have been given in the introduction.

crystals have the formula $C_{31}H_{24}O_4$, C_6H_6 , and rapidly effloresce when exposed to air. After heating for some time at 100° to expel the benzene of crystallisation, the substance melted at 200° and was indistinguishable from a specimen of anhydracetonedibenzil prepared by Japp and Miller.

Anhydracetonedibenzil is here formed according to the equation

Acetonebenzil and Benzaldehyde.—A mixture of 5 grams of acetonebenzil (Japp and Miller, Trans., 1885, 47, 22), 2 grams of benzaldehyde, 0.25 gram of caustic potash, and 60 c.c. of absolute alcohol was allowed to stand for over a fortnight. The solution, which was clear to start with, gradually deposited a yellow, crystalline substance, which, after recrystallisation from boiling alcohol, in which it was only sparingly soluble, formed minute, yellow, six-sided laminæ melting at 229°. It was identical with benzylideneanhydracetonebenzil, the condensation compound of benzaldehyde with anhydracetonebenzil. In the present case, it is formed according to the equation

$$C_{17}H_{16}O_8 + C_6H_5$$
·CHO = $C_{24}H_{18}O_2 + 2H_2O$.
Acetonebenzil. Benzylideneanhydracetonebenzil.

Benzil and Benzylideneacetons.—5 grams of benzil, 4 grams of benzylideneacetone, 0.25 gram of caustic potash, and 60 c.c. of absolute alcohol were used. The whole went into solution in a few hours, after which a yellow solid began to separate. This was filtered off after twelve days, washed with ether, and the resulting substance, which weighed 4.6 grams, was recrystallised from boiling alcohol, from which it was deposited in yellow needles melting at 200° . Analysis gave figures agreeing with the formula $C_{24}H_{18}O_{2}$.

This compound is desylenebenzylideneacetons
$$C_6H_5\cdot C:CH\cdot CO\cdot CH:CH\cdot C_6H_5$$
. $C_6H_5\cdot CO$

When heated in a test-tube in the vapour of diphenylamine, or when its hot alcoholic solution is mixed with alcoholic ammonia, or when alcoholic hydrochloric acid is allowed to act on it for a long time in the cold, it changes into the isomeric benzylideneanhydracetonebenzil. In like manner, when boiled for a few minutes with fuming hydriodic acid, it yields the compound $C_{24}H_{18}O$ (m. p. 182°) obtained by the reduction of benzylideneanhydracetonebenzil (vide supra).

CHEMICAL DEPARTMENT,
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C.—Triphenyloxazolone.

By Francis R. Japp, F.R.S., and Alexander Findlay, M.A., B.Sc. Japp and Murray (Trans., 1893, 63, 469) prepared oxazoles by the action of strong sulphuric acid in the cold on a mixture of a nitrile with benzoin:

$$R \cdot CN + \frac{CH(OH) \cdot C_6H_5}{CO \cdot C_6H_5} = R \cdot C \leqslant_{N \cdot C}^{O \cdot C_1 \cdot C_6H_5} + H_2O.$$

It occurred to us that, by substituting an a-hydroxy-acid for the a-keto-alcohol in the foregoing reaction, it might be possible to prepare oxazolones (ketodihydro-oxazoles); and on making the experiment with a mixture of benzonitrile and benzilic acid, we obtained the expected *triphenyloxazolone*:

$$\mathbf{C_6H_5 \cdot CN} \ + \ \frac{\mathbf{C}(\mathbf{OH})(\mathbf{C_6H_5})_2}{\mathbf{COOH}} \ = \ \mathbf{C_6H_5 \cdot C} \\ \stackrel{\bullet}{\leqslant} \mathbf{N \cdot CO} \ + \ \mathbf{H_2O}.$$

It melts at 136°.

At the same time, benzimidoxydiphenylacetic acid,

 $C_6H_5 \cdot C(NH) \cdot O \cdot C(C_6H_5)_2 \cdot COOH$

(m. p. 190°), was formed. This substance is not, as might at first sight appear, an intermediate product in the formation of triphenyloxazolone, inasmuch as concentrated sulphuric acid does not convert it into the latter compound, but, on the contrary, hydrolyses the oxazolone to the acid.

Heating with acetic anhydride converts the acid into the oxazolone, whilst boiling with *dilute* caustic potash transforms the oxazolone into a salt of the acid.

On heating the acid alone, it yields a mixture of the oxazolone and benzimidobenzhydrylic oxide, $C_6H_5\cdot C(NH)\cdot O\cdot CH(C_6H_5)_2$. The latter compound, which melts at 172—173°, and is formed from the acid with elimination of carbon dioxide, may be obtained as sole product by heating the acid with strong caustic potash. Its constitution was proved by its synthesis from benzonitrile and benzhydrol under the influence of gaseous hydrogen chloride. It thus belongs to the class of imido-ethers discovered by Pinner and Klein (Ber., 1877, 10, 1889), but differs from those hitherto described in its extraordinary stability.

Both the exazolone and the acid are decomposed by boiling for a few minutes with fuming hydriodic acid, the products in both cases being benzamide and diphenylacetic acid, the latter being, of course, formed by the reduction of the liberated benzilic acid. Benzimide-benzhydrylic exide, when treated with hydriodic acid, yields diphenylmethane in place of diphenylacetic acid.

By heating benzilic acid with benzamide, we obtained triphenyloxazolone, benzimidodiphenylacetic acid, and benzimidobenzhydrylic oxide, but all of them in only very small quantity.

Of the various other nitriles and a-hydroxy-acids with which we experimented, none gave reactions corresponding with those of benzonitrile and benzilic acid. By the action of concentrated sulphuric acid on a mixture of benzonitrile and lactic acid, we obtained a crystalline compound melting at 204—205°; but this, on analysis, proved to be ethylidenedibenzamide, CH₈·CH(NH·CO·C₆H₈)₂, which Hepp and Spiess (Ber., 1876, 9, 1425) prepared by the action of concentrated sulphuric acid on a mixture of aldehyde and benzonitrile. The lactic acid employed in our reaction had therefore yielded the aldehyde necessary for the formation of this compound.

EXPERIMENTAL.

Preparation of Triphenyloxazolone and Benzimidoxydiphenylacetic Acid.—10 grams of benzilic acid and an equal weight of benzonitrile were warmed until the whole became fluid, cooled, and poured slowly into 80 grams of concentrated sulphuric acid, stirring constantly and cooling with water. As soon as everything had dissolved, the solution was poured into water. The precipitated solid substance was filtered, pressed, to free it from adhering benzonitrile, and extracted with warm sodium carbonate solution, which removed organic acids. The residue was dissolved in hot ethylic acetate, from which it was deposited in large, transparent rhombs melting at 136°. It is only sparingly soluble in benzene, alcohol, and glacial acetic acid. Analysis gave figures agreeing with the formula of triphenyloxazolone, $C_6H_5 \cdot C \subset C(C_6H_5)_2$.

0·1282 gave 0·3762 CO₂ and 0·0574 H₂O. C=80·03; H=4·97. 0·1534 ,, 0·4524 CO₂ ,, 0·0703 H₂O. C=80·43; H=5·09. 0·2850 ,, 11 c.c. moist nitrogen at 15° and 772 mm. N=4·59.
$$C_{21}H_{16}NO_2$$
 requires C=80·51; H=4·79; N=4·47 per cent.

On acidifying the sodium carbonate extract, a solid was precipitated. This was boiled with water, which removed some unchanged benzilic acid. The residue could be recrystallised either from methylic alcohol

or from ethylic acetate. It was obtained in lustrous prisms or plates melting, with evolution of gas, at 190° . It is sparingly soluble in ethylic alcohol and in benzene. Analyses agreed with the formula of benzimidoxydiphenylacstic acid, $C_6H_5 \cdot C(NH) \cdot O \cdot C(C_6H_8)_{\circ} \cdot COOH$.

0.1850 gave 0.5146 CO₂ and 0.0894 H_2O . C = 75.86; H = 5.37. 0.4580 ,, 16.6 c.c. moist nitrogen at 15.5° and 772.5 mm. N = 4.30. $C_{21}H_{17}NO_2$ requires C = 76.13; H = 5.14; N = 4.23 per cent.

The silver salt was obtained as a white precipitate by adding silver nitrate to a solution of the ammonium salt. It is slightly soluble in boiling water.

0.1120 gave 0.0275 Ag. Ag = 24.55. $C_{31}H_{16}NO_8Ag$ requires Ag = 24.58 per cent.

The yield of acid and of oxazolone varies with the time during which the mixture of benzilic acid, benzonitrile, and sulphuric acid is allowed to stand before pouring it into water. The shorter this time is, the larger is the yield of oxazolone and the smaller that of acid.

Conversion of the Oxazolone into the Acid.—This change can be effected in various ways. Thus, when the oxazolone is dissolved in cold concentrated sulphuric acid, allowed to stand for some time, and then poured into water, the acid is precipitated—an observation which accounts for the diminished yield of oxazolone when the mixture is allowed to stand, even for a few minutes, in the preparation of these compounds.

The same change is produced when the oxazolone is boiled with glacial acetic acid to which a few drops of water have been added.

The change is best brought about, however, by boiling with caustic potash dissolved in ten times its weight of water. A reflux condenser should be used, as, if the water is allowed to evaporate, the concentrated alkali splits off carbon dioxide from the resulting acid. After boiling for $1-1\frac{1}{2}$ hours, a clear solution is obtained, which, on acidifying, gives a quantitative yield of the acid. After recrystallisation from methylic alcohol, it showed the correct melting point.

Conversion of the Acid into the Oxazolone.—The acid was heated with a mixture of acetic anhydride and fused potassium acetate for $1\frac{1}{3}$ hours at $150-160^{\circ}$. On cooling, the liquid had deposited crystals of the oxazolone, which, after recrystallisation from ethylic acetate, melted at $135-136^{\circ}$.

The conversion of the acid into the oxazolone also occurs when it is heated alone above its melting point, but in this case another decomposition occurs simultaneously. A weighed quantity of the

acid was introduced into a small tubulated distilling flask, which was then connected with a Sprengel pump, exhausted, and heated in a glycerol bath at $200-210^{\circ}$. The gas which was evolved was pumped off and collected in a measuring tube; it proved to be pure carbon dioxide. The residue in the flask was weighed, and then dissolved in ethylic acetate. The solution first deposited needles of benzimido-benzhydrylic oxide, $C_{20}H_{17}NO$ (vide infra), melting at 172° , and on further evaporation, crystals of the oxazolone melting at 135° . The volume of carbon dioxide evolved, and the loss in weight on heating, showed that exactly half of the acid had broken up into carbon dioxide and the compound $C_{20}H_{17}NO$, and half into water and the oxazolone $C_{21}H_{15}NO_2$. This ratio was, however, doubtless a mere coincidence.

Action of Hydriodic Acid on Benzimidoxydiphenylacetic Acid and on Triphenyloxazolons.—Benzimidoxydiphenylacetic acid was boiled for about 5 minutes with excess of the strongest hydriodic acid in an open flask. The product was poured into water, the separated solid dissolved in ether, the solution shaken with sulphurous acid, and then with a solution of sodium carbonate. On evaporating the ether a substance was left which from its melting point and other physical properties was recognised as benzamide.

On acidifying the sodium carbonate solution, an acid was precipitated. It was recrystallised from boiling water, and separated in colourless needles which melted at 145—146°. (M. p. of diphenylacetic acid 146°.) Analysis also gave figures agreeing with the formula of diphenylacetic acid.

0.1619 gave 0.4677 CO_2 and 0.0866 H_2O . C = 78.78; H = 5.94. $C_{14}H_{12}O_2$ requires C = 79.24; H = 5.66 per cent.

The oxazolone, when treated in the same way, gave the same products.

Action of Strong Caustic Potash on Benzimidoxydiphenylacetic Acid. —The acid was heated with a 33 per cent. solution of caustic potash in a nickel basin, evaporating to a small bulk. Water was then added, and the mixture boiled and filtered from the insoluble organic substance which had separated. On recrystallising this substance from ethylic acetate, it separated in colourless needles, melting at 172°. It is only slightly soluble in benzene, alcohol, and glacial acetic acid. Analysis showed that it had the formula $C_{e0}H_{17}NO$.

0.1539 gave 0.4701 CO_2 and 0.0855 H_2O . C = 83.31; H = 6.17. 0.1344 , 0.4115 CO_2 , 0.0740 H_2O . C = 83.50; H = 6.12.

0·1344 ,, 0·4115 CO_2 ,, 0·0740 H_2O . C = 83·50; H = 6·12. 0·1994 ,, 8·6 c.c. moist nitrogen at 15° and 765·5 mm. N = 5·08. $C_{20}H_{17}NO$ requires C = 83·62; H = 5·92; N = 4·88 per cent. The compound is thus formed from the acid by elimination of carbon dioxide. It is benzimidobenzhydrylic oxide, $C_6H_5 \cdot C(NH) \cdot O \cdot CH(C_6H_5)_2$. It has no basic properties.

It is not acted on by nitrous acid, or by a mixture of acetic anhydride and fused potassium acetate at 150°, or by sodium in boiling alcoholic solution, even when amylic alcohol was used. By boiling it however, with the strongest hydriodic acid, it was hydrolysed and reduced, and from the product of the reaction we succeeded in isolating diphenylmethane in colourless needles melting at 25—26°. The quantity was insufficient for analysis. Benzamide was not detected in the reduction as in the previous cases, but it was probably hydrolysed to benzoic acid which was volatilised during the boiling.

Synthesis of Benzimidobenzhydrylic Oxide from Benzonitrile and Benzhydrol.*—The constitution $C_0H_5 \cdot C(NH) \cdot O \cdot CH(C_0H_5)_2$, which we ascribe to this compound and which is expressed by the name benzimidobenzhydrylic oxide, would represent it as belonging to the class of imido-ethers discovered by Pinner and Klein (loc. cit.). The indifference of this compound towards acetic anhydride and other reagents which act on the imido-ethers hitherto known was, however, so great as to make us doubtful whether it really had this constitution. But its synthesis by the general reaction employed by Pinner and Klein—action of hydrogen chloride on a mixture of a nitrile and an alcohol—which we now describe, disposes of this doubt, and makes it clear that the compound is an imido-ether.

3 grams of benzhydrol and nearly 2 grams of benzonitrile were dissolved in dry ether, and the mixture saturated with gaseous hydrogen chloride, and allowed to stand in a corked flask for nearly a fortnight. The ether was then evaporated off, and the unchanged benzonitrile removed by distillation under reduced pressure. The residue was dissolved in alcohol, and precipitated by water; this caused it to separate as an oil, which partly crystallised on standing. By draining on a porous tile and recrystallising from ethylic acetate, the substance was obtained in needles melting at 170°, identical with the compound formed by the action of strong potash on benzimidoxy-diphenylacetic acid. The melting point was slightly low, but the quantity of substance was insufficient for further purification.

By heating a mixture of benzhydrol and benzonitrile in a U-tube at 110—120° and bubbling gaseous hydrogen chloride through the mixture

^{*} The benzhydrol employed was obtained by reducing benzophenone, dissolved in boiling alcohol, with an equal weight of sodium. The product was precipitated with water, distilled under reduced pressure, recrystallised from dilute alcohol, and finally dried on a porous plate. The yield of pure benzhydrol from 50 grams of benzophenone was only 25 grams, so that the process, although more expeditious than that of reducing with sodium amalgam, may possibly be less economical.

for 15 minutes, a slightly better yield of the compound was obtained. It showed the correct melting point of 172—173°. A nitrogen determination made with the rather small quantity of 0.1108 gram gave N=5.24 per cent. Calculated for $C_{20}H_{17}NO:N=4.88$ per cent.

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CI.—Interaction of Phenanthraquinone, Acetophenone, and Ammonia.

By Francis R. Japp, F.R.S., and Andrew N. Meldrum, B.Sc.

JAPP AND STREATFEILD showed (Trans., 1882, 41, 270) that phenanthraquinone, acetone, and ammonia interact according to the equation $C_{14}H_8O_2 + C_8H_6O + NH_8 = C_{17}H_{16}NO_2 + H_2O$, and to the compound thus formed the constitution $C_6H_4 \cdot C(OH) \cdot CH_2 \cdot CO \cdot CH_8$ was assigned by $C_6H_4 \cdot C:NH$

Japp and Miller (Trans., 1885, 47, 12). The results of the present investigation, however, lead us to ascribe to it rather the constitution of an acetonylaminophenanthrone, $\begin{array}{c} C_0H_4 \cdot C(NH_2) \cdot CH_2 \cdot CO \cdot CH_3, \\ C_0H_4 \cdot CO \end{array}$, analogous acetonylaminophenanthrone, $\begin{array}{c} C_0H_4 \cdot C(NH_2) \cdot CH_2 \cdot CO \cdot CH_3, \\ C_0H_4 \cdot CO \end{array}$

gous to that of diacetonamine, $(CH_3)_2C(NH_2)\cdot CH_2\cdot CO\cdot CH_3$. Thus we find that phenanthraquinone, acetophenone, and alcoholic ammonia interact according to the equation

yielding diphenacyldiaminodihydrophenanthrens. It is evident that a constitution analogous to that ascribed by Japp and Miller to the acetone-ammonia derivative is inadmissible in the case of this compound.

The acetophenone-ammonia derivative is hydrolysed by aqueous oxalic acid according to the equation

yielding phenacylhydroxyphenanthrone (acetophenonephenanthraquinone) which melts at 125—130°.

By the interaction of phenanthraquinone, acetophenone, and aqueous

ammonia, phenacylaminophenanthrone, $C_6H_4 \cdot C(NH_2) \cdot CH_2 \cdot CO \cdot C_6H_5$,

analogous to the acetone-ammonia derivative, was obtained. The same substance is formed by the action of ammonia on phenacylhydroxyphenanthrone.

The ease with which these compounds break up into their generating substances rendered a detailed study of their reactions impossible.

Other ketones, such as methyl ethyl ketone and diethyl ketone, appeared to act in a similar manner with phenanthraquinone and ammonia; but it was found impossible to obtain the resulting compounds in a condition suitable for analysis.

EXPERIMENTAL.

Action of Alcoholic Ammonia on a Mixture of Phenanthraquinone and Acetophenone. -20 grams of phenanthraquinone, 28 grams of acetophenone, and a large excess of alcoholic ammonia were heated in an open flask on the water-bath. In proportion as the ammonia was expelled and the boiling point of the mixture rose, the greater part of the phenanthraquinone passed into solution. The filtered liquid deposited, on cooling, yellow, lustrous needles, which, by their appearance and melting point (158-159°), were recognised as phenanthraquinonimide. Later on, a colourless substance began to separate. The liquid was therefore again filtered, and, on standing overnight, deposited a large quantity of this second substance in tufts of colourless, silky needles, which, when heated in a capillary tube, decomposed about 150°, without showing a definite melting point. In some preparations of this substance, the portions first deposited showed a pinkish tinge; but, by filtering at this stage, the colourless substance was obtained from the filtrate. As we found it impossible to recrystallise this substance without decomposing it, it was merely washed with cold alcohol, and dried for analysis in a vacuum desiccator. perfectly homogeneous in appearance.

Analysis gave figures agreeing with the formula of diphenacyldiaminodihydrophenanthrens, $C_6H_4 \cdot C(NH_2) \cdot CH_2 \cdot CO \cdot C_6H_5$. $C_6H_4 \cdot C(NH_2) \cdot CH_2 \cdot CO \cdot C_6H_5$

0.1570 gave 0.4657 CO₂ and 0.0794 H₂O. C=80.90; H=5.62. 0.1454 , 0.4317 CO₂ , 0.0738 H₂O. C=80.98; H=5.64. 0.3049 , 16.2 c.c. moist nitrogen at 11° and 740 mm. N=6.17. 0.2928 , 15.5 , , 13° , 754 mm. N=6.20. $C_{80}H_{20}N_{2}O_{2}$ requires C=80.72; H=5.83; N=6.28 per cent.

Hydrolysis of Diphenacyldiaminodihydrophenanthrens.—In this experiment, the method employed by Japp and Miller (loc. cit., p. 17) in VOL. LXXV.

the hydrolysis of acetonylaminophenanthrone to acetonephenanthraquinone, was followed. The diphenacyldiaminodihydrophenanthrene was first moistened with alcohol-since otherwise it is not readily wetted by water-ground with water to a thin cream, and then poured into a large excess of a cold concentrated aqueous solution of oxalic acid, stirring well. Almost everything dissolved. The solution was quickly filtered through a large folded filter-an operation which must be rapidly performed, as the separation of the new compound begins almost immediately—and the filtrate, which speedily became yellow and turbid and smelt strongly of acetophenone, was allowed to stand over night. There was a large deposit of a pale yellow substance; this was filtered off, thoroughly washed with water, dried in a vacuum desiccator, and purified by recrystallisation, first from ether, allowing the solvent to evaporate spontaneously, and afterwards from ethylic acetate, the latter giving the better result. It was thus obtained in fairly large thick prisms or six-sided plates which had a scarcely perceptible yellowish tinge, and are doubtless colourless when pure. melted between 125° and 130°, turning dark yellow. Boiling the substance with solvents must be avoided, as this treatment decomposes it.

Analysis gave figures agreeing with the formula of phenacylhydroxyphenanthrone (acetophenonephenanthraquinone),

As acetonephenanthraquinone, when boiled with fuming hydriodic acid, yields diphenylenemethylfurfuran (Trans., 1890, 57, 663), we subjected the foregoing compound to the same treatment, in the hope of obtaining a diphenylenephenylfurfuran, but found that it broke up, before reduction, into acetophenone and phenanthraquinone, the latter then yielding phenanthrone and tetraphenylenefurfuran.

By passing gaseous ammonia into an ethereal solution of phenacylhydroxyphenanthrone, we obtained *phenacylaminophenanthrone*, $C_6H_4 \cdot C(NH_2) \cdot CH_2 \cdot CO \cdot C_6H_5$. This compound is, however, more readily $C_6H_4 \cdot CO$

prepared by the method described in the next paragraph.

Action of Aqueous Ammonia on a Mixture of Phenanthraquinone and Acetophenone.—20 grams of phenanthraquinone, 14 grams of acetophenone, and an excess of the strongest aqueous ammonia were introduced into a strong flask; this was tightly corked, and the mixture shaken vigorously, at intervals, during several hours. The organic substance solidified in the form of yellowish granules, whilst the

aqueous portion was red. The solid substance was separated, ground with water, thoroughly washed, and dried over sulphuric acid. It was then digested with a small quantity of chloroform in the cold, to remove unaltered phenanthraquinone, after which the residue was treated with sufficient cold chloroform to dissolve nearly the whole. On adding light petroleum to the filtered chloroform solution, a bulky, white precipitate was obtained; this was filtered off and dried at the ordinary temperature. The substance, which was yellowish after drying, was dissolved in cold ether which had been previously saturated with ammonia (in order to check the tendency of the substance to decomposition), and the solution was allowed to evaporate spontaneously. In this way, the compound was obtained in small, colourless, six-sided plates, which melted with decomposition about 160°, turning green and evolving gas. The loss in purification by the above method is very great. Heating with solvents decomposes the substance completely.

Analysis gave figures pointing to the formula of a phenacylaminophenanthrone, $C_6H_4\cdot C(NH_2)\cdot CH_2\cdot CO\cdot C_6H_5$. The substance was diffi-

cult to burn, and the value for carbon was low.

0.1175 gave 0.3449 CO, and 0.0570 H_2O . C = 80.05; H = 5.39. 0.3090 , 11.7 c.c. moist nitrogen at 18° and 754 mm. N=4.33. $C_{e_2}H_{17}NO_{e_1}$ requires C = 80.73; H = 5.20; N = 4.28 per cent.

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CII.—Furfuran Derivatives from Benzoin and Phenols.

By Francis R. Japp, F.R.S., and Andrew N. Meldrum, B.Sc.

By the action of cold, concentrated sulphuric acid on a mixture of benzoin and phenol, Japp and Wadsworth (Trans, 1890, 58, 965) obtained paradesylphenolsulphonic acid, from which, by hydrolysing it with strong hydrochloric acid at 150°, paradesylphenol,

$$C_6H_6 \cdot CH \cdot C_6H_4 \cdot OH_{(1:4)},$$
 $C_6H_6 \cdot CO$

was prepared.

We now find that by heating a mixture of benzoin and phenol with sulphuric acid of 73 per cent. strength,* the foregoing condensation occurs without sulphonation of the resulting compound, and an

^{*} Corresponding with the hydrate H₂SO₄, 2H₂O. A sulphuric acid of this strength was first used for condensations by Bistrzycki and Oehlert (Ber., 1894, 27, 2682).

excellent yield of paradesylphenol is obtained. The various condensations about to be described were effected by means of sulphuric acid of this strength.

If the desyl group were to take up the ortho-position towards the hydroxyl of the phenol, it is evident that, by a further elimination of water, a furfuran derivative might be formed:

With phenol and benzoin, no such reaction occurs: the para-compound alone is formed. With thymol and benzoin, however, a mixture of desylthymol and cymodiphenylfurfuran is obtained. In the case of resorcinol and of quinol, either one or two diphenylfurfuran groups may be introduced. With phloroglucinol, only the compound containing three such groups was obtained.

Up to a certain point these reactions resemble those studied by Hantzsch and his pupils (Ber., 1886, 19, 1290, 2927, and 2934), in which furfuran derivatives were obtained by the action of ethylic a-chloracetoacetate on the sodium compounds of phenols. with phenol, a benzomonofurfuran derivative was thus prepared; whilst from di- and tri-hydroxybenzenes, compounds containing either one, or two, or three furfuran groups were obtained, just as in the reactions described in the present paper. But there is an important distinction to be drawn between the mechanisms of the two sets of reactions. In Hantzsch's reactions, the first stage is the formation of an ether of the phenol in question—thus of ethylic a-phenoxylacetoacetate in the first of the syntheses referred to—and the linking of carbon to earbon is a subsequent process. In the reactions here described, the first stage is the linking of the desyl group to the nucleus of a phenol, whilst the closing of the furfuran ring by oxygen follows. Were this otherwise, phenol and benzoin would yield only diphenylbenzofurfuran, instead of, as actually happens, only paradesylphenol.

We may mention that the present research was completed last year, before the publication of Graebe's investigation of benzoin yellow (Ber., 1898, 31, 2975), in which it is shown that, by the action of sulphuric acid on a mixture of benzoin and gallic acid, a compound containing a diphenylfurfuran group is formed.

EXPERIMENTAL.

1. Benzoin and Phenol.

20 grams of benzoin, 9 grams of phenol,* and 80 grams of 73 per cent. sulphuric acid were heated by means of an oil-bath at 120—150° for 20 minutes, frequently shaking the flask. The product, which was dark-coloured, was allowed to cool, the aqueous portion was poured off, and the organic substance was boiled, first with water and then with a solution of sodium carbonate, after which it was recrystallised from a mixture of benzene and light petroleum. It melted constantly at 133° and exhibited all the other properties of paradesylphenol (Trans., 1890, 57, 966). The yield was good, and the method is a great improvement on that previously described (loc. cit.).

Afterwards, when we had ascertained that various other phenols yielded furfuran derivatives, a second preparation of the foregoing compound was made in order to ascertain whether any benzodiphenyl-furfuran was formed at the same time. For this purpose, the operation was conducted as just described, except that the crude product, after extraction with sodium carbonate, was dissolved in ether, and the solution shaken with dilute caustic soda as long as the latter removed anything. Any benzodiphenylfurfuran would thus remain behind in the ether; but, on evaporating the ethereal liquid, only a small quantity of an uncrystallisable resin was obtained, closely resembling the product of the action of sulphuric acid on benzoin alone.

2. Benzoin and Thymol.

20 grams of benzoin and 40 grams of thymol were melted together, 80 grams of 73 per cent. sulphuric acid were added, and the mixture was heated, with shaking, for 20 minutes at 150—170°. The viscid product was washed with water, and then steam-distilled as long as any thymol passed over. The dark-coloured solid which remained was dissolved in boiling alcohol. The filtered solution deposited, on cooling, a resinous substance; the liquid, poured off from this, gave, on standing, cauliflower-like aggregates of crystals (A). The filtrate from these contained, along with much resin, a very soluble, crystalline substance: this was obtained, by crystallisation from a mixture of alcohol and light petroleum, in colourless laminæ melting at 126°. It is readily soluble in alcohol and benzene, sparingly soluble in light petroleum. Analysis gave figures agreeing with the CoH₅·CH·C₆H₂(CH₃)(C₃H₇)OH formula of a desylthymol, CoH₅·CO

^{*} From our experience with other phenols, it is probable that the employment of an excess of phenol in this experiment would have given a still better result.

The position of the desyl group is uncertain, except that it is doubtless not contiguous to the hydroxyl, otherwise the compound would be converted, with elimination of water, into cymodiphenylfurfuran.

Although desylthymol contains a phenolic hydroxyl group, it is almost insoluble in aqueous caustic alkali. A similar phenomenon has been observed in the case of Mazzara's benzylthymol and dibenzylthymol (Abstr., 1882, 42, 171), which are, however, quite insoluble in aqueous caustic alkali, although the benzyl groups replace hydrogen of the nucleus. In the case of desylthymol, the addition of a very little alcohol to the aqueous caustic alkali causes the substance to dissolve—a property which might possibly be utilised in separating it from the cymodiphenylfurfuran (vide infra) formed along with it in the process of preparation.

The presence of a hydroxyl group in desylthymol may be readily proved by boiling the compound with acetic anhydride, when it forms a monacetyl derivative which crystallises from alcohol in colourless needles, melting at 110°. On analysis, it gave figures agreeing with the formula of acetyldesylthymol, $C_6H_5\cdot CH\cdot C_6H_2(CH_3)(C_8H_7)O\cdot C_2H_3O$.

0.1503 gave 0.4431 CO₂ and 0.0918 H₂O.
$$C = 80.40$$
; H = 6.79. $C_{26}H_{26}O_3$ requires $C = 80.83$; H = 6.74 per cent.

The cauliflower-like aggregates of crystals (substance A, vide supra), obtained in the crystallisation of the crude product of the condensation, were washed with cold, and then recrystallised from hot, alcohol. As they were found to contain alcohol of crystallisation, which was difficult to expel completely, they were recrystallised from light petroleum. In this way, the substance was obtained in tufts of slender needles melting at 115—116°. It sublimes slowly when heated on the waterbath. It gave figures agreeing with the formula of a cymodiphonylfur-

furan,
$$CH_8$$
 $C \cdot C_6H_5$
 $C \cdot C_6H_5$

0.1895 gave 0.6109 CO₂ and 0.1171 H₂O. C = 87.92; H = 6.87. 0.1614 ,, 0.5208 CO₂ ,, 0.1007 H₂O. C = 88.00; H = 6.93. $C_{24}H_{22}O$ requires C = 88.34; H = 6.74 per cent.

3. Benzoin and Pyrocatechol.

The dihydric phenols interact either with one or with two molecules of benzoin, yielding respectively mono- and di-furfuran derivatives. The former are soluble, the latter insoluble, in caustic alkalis.

The result obtained with pyrocatechol was so unsatisfactory that we refrain from describing in detail the process employed. The greater part of the product dissolved in caustic soda, but the reprecipitated substance was so readily oxidisable that we were unable to purify it. A small portion, insoluble in caustic soda, was recrystallised from benzene, and was thus obtained in tufts of slender needles melting at 237°. The results of analysis left no doubt that it had the expected formula $C_{24}H_{22}O_{2}$, but the values for carbon were low, and the quantity of substance was insufficient for further purification. Found: C, 87.69, 87.53; H, 4.83, 4.80. Calculated: C, 88.31; H, 4.76 per cent.

Judging by the results obtained with the other dihydric phenols, the compound is orthobenzotetraphenyldifurfuran,

$$C_{\theta}H_{\delta}\cdot C C_{\theta}H_{\delta}.$$

4. Benzoin and Resorcinol.

In the reactions with the dihydric phenols, it was found advantageous to employ different proportions of the interacting substances according as the mono- or the di-furfuran derivative was required. In the former case, a large excess of the phenol—3 mols. of the latter to 1 of benzoin—was used; in the latter, equimolecular proportions of the two substances—this being again an excess of the phenol, from the point of view of the desired reaction—gave the best result.

 $\textit{Metahydroxybenzodiphenylfurfuran}, \ C_6H_3(OH) < \begin{matrix} C(C_6H_5) \\ C \end{matrix} \cdot \begin{matrix} C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ C_6H_5 \end{matrix} \cdot \begin{matrix} C \\ 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40 grams of benzoin and 62 grams of resorcinol were melted together, 160 grams of 73 per cent. sulphuric acid were added, and the mixture was heated, with shaking, for 15 minutes at 120—130°. The dark coloured product, which solidified on cooling, was washed with water, and boiled with dilute caustic soda, in which it nearly all dissolved. The filtered solution deposited a sodium salt in six-sided lamins with a satiny lustre; these, when filtered off, cohered, forming a greasy mass. As the salt was pink coloured, it was recrystallised from boiling water, with the addition of a little caustic soda to prevent the hydrolysis which otherwise occurs, until it was practically colourless. It gives a colourless, aqueous solution with a yellowish-green fluorescence, resembling that of uranium glass. It contains

water of crystallisation, which is entirely driven off at 110° . The anhydrous salt gave, on analysis: Na = 7.86. Required for $C_{20}H_{13}O_3Na$: Na = 7.47 per cent. The excess was doubtless due to the fact that the substance was deposited from a solution containing caustic soda. The substance could not be contaminated with the sodium compound of resorcinol, as that compound is very readily soluble in cold water, whereas the new sodium salt is only sparingly soluble. The potassium salt, on the contrary, is readily soluble.

In order to obtain the phenolic substance, the sodium salt was dissolved in hot, dilute alcohol, and the boiling solution was acidified and poured into excess of boiling water. The organic substance separated as a dark coloured, thick oil, which did not solidify on standing. Its purification presented difficulties, owing to the tendency of the substance to separate in an amorphous form from its solutions. It was finally purified, although not without considerable loss, by dissolving it in chloroform and adding light petroleum gradually, so as to precipitate resinous impurities; the colourless solution thus obtained yielded tufts of white needles with a satiny lustre, melting constantly at 117.5° . It is readily soluble in most organic solvents; the alcoholic solution shows a violet fluorescence. Analysis gave figures agreeing with the formula of metahydroxybenzodiphenylfurfuran, $C_6H_3(OH) \swarrow_{O(C_6H_5): C^{\circ}C_6H_5}$.

0.2084 gave 0.6389
$$CO_2$$
 and 0.0969 H_2O . $C = 83.61$; $H = 5.16$. 0.1516 , 0.4655 CO_2 , 0.0687 H_2O . $C = 83.74$; $H = 5.03$. $C_{20}H_{14}O_2$ requires $C = 83.92$; $H = 4.89$ per cent.

Of the two possible isomeric hydroxybenzodiphenylfurfurans derivable from resorcinol, only the foregoing was observed. Judging

from analogy, its constitution is probably
$$HO$$
 $C \cdot C_0H_5$.

Acetyl Derivative.—4 grams of the foregoing substance were boiled with 6 grams of acetic anhydride for 2 hours, and the resulting acetyl derivative was purified by recrystallisation, first from a mixture of benzene and light petroleum, then from alcohol, from which it was deposited in slender prisms melting at 117°. The practical coincidence of the melting point with that of the original compound is anomalous, inasmuch as acetyl derivatives in which acetyl replaces hydrogen of a hydroxyl group generally melt much lower than the hydroxy-compounds.

Analysis of the substance, dried at 100°, gave figures agreeing with the formula of metacetoxybenzodiphenylfurfuran,

$$\mathbf{C_6H_3}(\mathbf{OC_2H_3O}) \diagdown \mathbf{C(\underline{C_6H_5):C \cdot C_6H_5}}.$$

0.2314 gave 0.6821 CO₂ and 0.1078 H₂O. C = 80.39; H = 5.18. $C_{22}H_{16}O_3$ requires C = 80.49; H = 4.88 per cent.

 $C_6H_2\left[\begin{array}{c} C(C_6H_5):C\cdot C_6H_5 \\ O \end{array}\right]_a . -10$ Metabenzotetraphenyldifurfuran, grams of benzoin and 10 grams of resorcinol were melted together, 80 grams of 73 per cent. sulphuric acid were added, and the mixture was heated at 160° for 15 minutes, shaking it from time to time, and gradually adding a further 10 grams of benzoin. The melt, which became very tarry, was cooled, washed with water, and boiled with strong caustic soda; the mixture was then diluted with water, and filtered hot, so as to remove phenolic compounds. The insoluble residue was boiled up with a little alcohol, allowed to cool, and then filtered; this removed a considerable amount of colouring matter. The substance was then crystallised several times from hot benzene, from which it was deposited in short, oblique prisms or plates, containing benzene of crystallisation, and finally from hot glacial acetic acid, from which it separated in tufts of colourless, slender needles, melting at 217-219°. It is fairly soluble in hot benzene or glacial acetic acid, readily soluble in chloroform, only sparingly soluble in alcohol. All the solutions showed a violet fluorescence. Analysis gave figures agreeing with the formula of metabenzotetraphenyldifurfuran, $\mathbf{C_6H_2} \begin{bmatrix} \mathbf{C}(\mathbf{C_6H_5}) : \mathbf{C} \cdot \mathbf{C_6H_5} \end{bmatrix}_{\alpha}$

5. Benzoin and Quinol.

Parahydroxybenzodiphenylfurfuran,

$$\begin{array}{c} \text{HO} \\ \begin{array}{c} \text{C} \cdot \text{C}_6 \text{H}_5 \\ \text{C} \cdot \text{C}_6 \text{H}_5 \cdot -20 \end{array}$$

grams of benzoin and 31 grams of quinol were melted together, 80 grams of 73 per cent. sulphuric acid were added, and the whole was heated, with shaking, at 120—150° for about 20 minutes, gradually raising the temperature. The solid product was powdered and then thoroughly extracted with boiling water to remove quinol. It was then treated exactly like the corresponding resorcinol derivative, by dissolving it in caustic soda (when a considerable residue of parabenzotetraphenyl-difurfuran remained undissolved), purifying the sodium salt by recrys-

tallisation, liberating the phenolic compound, and purifying the latter by recrystallisation, first from a mixture of benzene and light petroleum, then from chloroform and light petroleum. It was thus obtained in rosettes of colourless, flat needles melting at 158—160°. It crystallises much more readily than the meta-compound. Analysis gave figures agreeing with the formula of parahydroxybenzodiphenyl-furfuran.

Acetyl Derivative.—Half a gram of the foregoing compound was boiled with 2 grams of acetic anhydride for 2 hours, and the product recrystallised from alcohol. It formed laminæ, melting at 137°. Analysis showed that it was a monacetyl compound

0.1247 gave 0.3669 CO₂ and 0.0558 H₂O.
$$C = 80.24$$
; $H = 4.97$. $C_{22}H_{16}O_{3}$ requires $C = 80.49$; $H = 4.48$ per cent.

Parabenzotetraphenyldifurfuran, $C_6H_2\left[\frac{C(C_6H_5):C^{\bullet}C_6H_5}{O}\right]_2$.—20 grams of benzoin and 10 grams of quinol were melted together, 80 grams of 73 per cent. sulphuric acid were added, and the mixture was heated at 150° for 15 minutes with frequent shaking. The resinous mass thus obtained was powdered and boiled with alcohol; this gave a deep blue solution, from which nothing definite was obtained, and a white residue. The latter was purified by recrystallising it several times from benzene. It was thus obtained in clusters of needles melting at 278°. The benzene solution was strongly fluorescent, the crystals slightly so. Analysis gave figures agreeing with the formula of parabenzotetraphenyldifurfuran.

0.1828 gave 0.5897 CO₂ and 0.0821 H₂O. C=87.98; H=4.99.
0.1430 , 0.4619 CO₂ , 0.0623 H₂O. C=88.09; H=4.84.
$$C_{84}H_{29}O_2$$
 requires C=88.31; H=4.76 per cent.

Only the foregoing compound could be detected in the product of the reaction, although two isomerides are possible.

6. Benzoin and Phloroglucinol.

50 grams of benzoin, 10 grams of phloroglucinol, and 80 grams of 73 per cent. sulphuric acid were taken, and the process was conducted as in the previous experiments. The heating was continued for 15 minutes at 150°. It is best to add the whole of the sulphuric acid at once to the melted mixture of benzoin and phloroglucinol; in one experiment in which only a little was added at first, a vigorous

reaction took place, steam was given off, and the substance turned very dark.

The dark brown product was boiled with water, with alcoholic sodium hydrate, again with water, then with alcohol alone, and finally with a small quantity of benzene. In this way, an almost white residue was obtained, which was recrystallised several times from solvent naphtha, and afterwards from benzene. It forms tufts of colourless, slender needles melting at 360°. During the purification, fluorescent solutions were obtained; but solutions of the pure substance are non-fluorescent. It is almost insoluble in alcohol, glacial acetic acid, and ethylic acetate; but chloroform dissolves it readily. Analysis gave figures agreeing with the formula of benzohexaphenyltrifurfuran, $C_6 \begin{bmatrix} C(C_6H_5) : C \cdot C_6H_5 \\ O \end{bmatrix}$.

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CIII.—Interaction of Benzoin with Phenylenediamines.

By Francis R. Japp, F.R.S., and Andrew N. Meldrum, B.Sc.

By heating benzoin with aniline and a little aniline hydrochloride, Japp and Murray (Trans., 1894, 65, 892) obtained 2':3'-diphenyl-indole. The desylanilide, C_6H_5 ·CO·CH(NH· C_6H_5)· C_6H_5 , which is formed in the first instance, and which is the sole product if aniline alone is used, parts with water under the influence of the hydrochloric acid, yielding the indole.

We have now studied this reaction with the phenylenediamines, in order, if possible, to obtain the corresponding benzodipyrrhole derivatives; but only in the case of metaphenylenediamine did the reaction take place in the desired sense.

1. Benzoin and Orthophenylenediamine.

By heating benzoin with orthophenylenediamine hydrochloride, phenylbenzimidazole hydrochloride, $C_6H_4 < NH > C \cdot C_6H_5$, HCl, was obtained, the benzoin molecule breaking up in the process. The free phenylbenzimidazole melted at 285° (instead of 291°).

Benzoin and free orthophenylenediamine, on the other hand, yielded diphenylquinoxaline, $C_6H_4 < N: C \cdot C_6H_5$, oxidation taking place during the process. The formation of the latter compound in this reaction had, as we afterwards found, been already observed by O. Fischer (Ber., 1891, 24, 720).

2. Benzoin and Metaphenylenediamine.

Ten grams of metaphenylenediamine hydrochloride were dissolved in water, and the base was liberated by caustic soda and extracted with ether. The ethereal solution was dried with potassium carbonate and the ether distilled off. To the base thus obtained 23 grams of benzoin were added, and the mixture was heated to 180°. No reaction occurred; but on adding a little metaphenylenediamine hydrochloride, there was a vigorous effervescence; water was given off, and the mass solidified in spite of the high temperature. By extracting the melt with boiling alcohol and recrystallising the residue from solvent naphtha, the new compound was obtained in slender needles melting at 282°. It is almost insoluble in alcohol and benzene, soluble in chloroform. Dilute acids do not dissolve it; but it is soluble in concentrated sulphuric acid, giving a faint red solution with a greenish fluorescence.

. Analysis gave figures agreeing with the formula of a metabenzo-tetraphenyldipyrrhole, $C_6H_2\begin{bmatrix} C(C_6H_5):C\cdot C_6H_5\\ NH \end{bmatrix}_2$.

0.1806 gave 0.5858 CO₂ and 0.0871 H₂O. C = 88.46; H = 5.36. 0.2604 ,, 13.1 c.c. moist nitrogen at 14° and 751 mm. N = 5.85. $C_{84}H_{24}N_{2}$ requires C = 88.70; H = 5.22; N = 6.09 per cent.

Two constitutions are possible for this compound, and at present there is apparently no means of deciding between them.

The same compound may be obtained by heating together benzoin and metaphenylenediamine hydrochloride, thus obviating the necessity of preparing the free base; but the yield is bad, and the substance difficult to purify.

3. Benzoin and Paraphenylenediamine.

The only method that yielded a definite product was that described in the case of the meta-compound: namely, of heating together benzoin and the free base, and adding a little of the hydrochloride.

Twelve grams of paraphenylenediamine hydrochloride were taken; the base was liberated and extracted with ether, of which a large quantity was required on account of the sparing solubility of the para-compound. The base which remained after distilling off the ether was heated along with 23 grams of benzoin until the whole melted. No action took place; but on gradually adding 3 grams of paraphenylene-diamine hydrochloride, the fused mass became pasty and ultimately solidified. The reaction was not so vigorous as in the case of the metacompound, and less water was given off. The product was boiled with alcohol, and the undissolved portion, which was yellow, was washed with boiling water, dried, and recrystallised from benzene. It was obtained pure by a single crystallisation, and formed bright yellow, minute laminæ which, when heated, showed signs of softening about 230° , and melted completely at 257° . Analysis pointed to the formula $C_{24}H_{28}N_{2}O_{2}$.

0.1846 gave 0.5588 CO₂ and 0.0954 H₂O. C = 82.55; H = 5.74. 0.2144 ,, 10.4 c.c. moist nitrogen at 12.5° and 743 mm. N = 5.62. $C_{34}H_{28}N_2O_2$ requires C = 82.26; H = 5.64; N = 5.64 per cent.

The compound is formed according to the equation

$$\begin{array}{lll} \mathbf{C_6H_4(NH_2)_2} &+& \mathbf{2_{CO \cdot C_6H_5}^{CH(OH) \cdot C_6H_5}} &=& \mathbf{C_6H_4} \begin{bmatrix} \mathbf{NH \cdot CH \cdot C_6H_5} \\ \mathbf{CO \cdot C_6H_5} \end{bmatrix}_{\circ} &+& \mathbf{2H_2O_5} \\ \mathbf{Paraphenylenediamine.} \end{array}$$

and may receive the name didesylparaphenylenediamine. It corresponds with desylanilide (anilbenzoin) and the other compounds obtained by Voigt by heating benzoin with primary benzenoid amines (compare Trans., 1894, 65, 890).

Diacetyl Derivative.—Two grams of the foregoing compound were boiled with excess of acetic anhydride for 10 minutes. The solution, which was light red at first and afterwards became darker, was allowed to cool, and ether was added. A white, crystalline substance separated, which was recrystallised from amylic alcohol, and was thus obtained in colourless, slender needles melting at 279°. Analysis gave figures agreeing with those required for didesylparaphenylene-

$$\begin{array}{ll} \textit{diacetdiamine,} & C_6H_4 \begin{bmatrix} N(C_2H_5O) \cdot CH \cdot C_6H_5 \\ CO \cdot C_6H_5 \end{bmatrix}_2. \end{array}$$

0.1217 gave 0.3507 CO_2 and 0.0616 H_2O . C = 78.59; H = 5.62. 0.1166 ,, 5.0 c.c. moist nitrogen at 14° and 758 mm. N = 5.03. $C_{38}H_{32}N_2O_4$ requires C = 78.62; H = 5.52; N = 4.83 per cent.

We tried to convert didesylparaphenylenediamine into the corresponding benzodipyrrhole derivative by heating it with zinc chloride. It is possible that this transformation does take place, but the product was a mixture of two substances (needles melting at \$18° and prisms melting at \$35°—both yellow coloured) of almost

equal solubility; so that, with the small quantity at our disposal, we were unable to separate them.

The foregoing five papers form a continuation of a general investigation of the reactions of ketonic compounds (compare Trans., 1897, 71, 123), and the expenses incidental to the work have for some years past been defrayed by various grants from the Government Grant Fund of the Royal Society.

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CIV.—A Series of Substituted Nitrogen Chlorides and their Relation to the Substitution of Halogen in Anilides and Anilines.

By F. D. CHATTAWAY and K. J. P. ORTON.

Compounds in which a halogen is attached to nitrogen have been little studied, although a number of isolated examples are known. Among such may be mentioned nitrogen chloride, nitrogen iodide, the chlorine derivatives of a few aliphatic amines (Tscherniak, Ber., 1876, 9, 143; Norton and Tscherniak, Bull. Soc. Chim., 1878, [ii], 30, 106), of acetanilide (Bender, Ber., 1886, 19, 2272), of benzamide (ibid.), of succinimide (ibid.), and of phenylnitramine (Bamberger, Ber., 1894, 27, 376), the bromine derivatives of the aliphatic amides (Hofmann, Ber., 1882, 15, 407 and 752), and of benzamilide (Linebarger, Amer. Chem. J., 1894, 16, 218), the iodine derivatives of succinimide (Bunge, Annalen Suppl., 1870, 7, 119), of acetamide (Seliwanow, Ber., 1893, 26, 985), and of formanilide (Comstock and Kleeberg, Amer. Chem. J., 1890, 12, 500), methylic and ethylic chlorimidocarbonates (Sandmeyer, Ber., 1886, 9, 862), and the chlorimide obtained from the oxime of benzophenone (Beckmann, Ber., 1886, 19, 988).

Some years ago, the attention of one of us was drawn to a substance obtained by Witt (Ber., 1875, 8, 1226) by the action of hypochlorous acid on acetanilide, and this was employed in a simple process for preparing metadichlorobenzene in quantity (Chattaway and Evans, Trans., 1896, 69, 848). In continuation of our work upon nitrogen iodide, we recently took up the study of this compound, and have obtained a series of substituted nitrogen chlorides which undergo remarkable intramolecular transformations and are of extreme interest from their bearing on the theory of substitution.

We find that, by the action of hypochlorous acid under carefully

regulated conditions, compounds of this nature can be obtained from most substances containing hydrogen attached to nitrogen.

In the present paper are considered the disubstitution products of nitrogen chloride containing formyl, acetyl, or benzoyl, together with a phenyl or chlorophenyl residue. These form a well-defined group of compounds, phenyl acetyl nitrogen chloride, discovered by Bender, being one of the simplest members. They are readily obtained from the corresponding formanilide, acetanilide, or benzanilide by interaction with hypochlorous acid.

$$R \cdot CO \cdot NR'H + HOCl = R \cdot CO \cdot NR'Cl + H_2O.$$

They are all stable compounds of low melting point, crystallising well in large, colourless, transparent prisms or plates, and reacting very readily with alcohol, hydrochloric acid, hydrocyanic acid, potassium iodide, and alkaline hydrogen peroxide.

(a) With alcohol, the anilide is reformed, and aldehyde, ethylic chloride, and other substances are liberated, ethylic hypochlorite, which breaks up into aldehyde and hydrochloric acid, being probably first produced.

$$\begin{aligned} \mathbf{R} \cdot \mathbf{CO} \cdot \mathbf{NR'Cl} + \mathbf{C_2H_5} \cdot \mathbf{OH} &= \mathbf{R} \cdot \mathbf{CO} \cdot \mathbf{NR'H} + \mathbf{C_2H_5} \cdot \mathbf{OCl}. \\ \mathbf{CH_8} \cdot \mathbf{CH_2} \cdot \mathbf{OCl} &= \mathbf{HCl} + \mathbf{CH_8} \cdot \mathbf{CHO}. \end{aligned}$$

(b) With strong hydrochloric acid, chlorine is set free and the anilide regenerated.

$$R \cdot CO \cdot NR'Cl + HCl = R \cdot CO \cdot NR'H + Cl_2$$

In some cases, however, under the influence of the acid, a portion of the compound undergoes an intramolecular transformation similar to that which takes place when it is heated.

(c) With hydrocyanic acid, the anilide and cyanogen chloride are formed.

$$R \cdot CO \cdot NR'Cl + HCN = CNCl + R \cdot CO \cdot NR'H.$$

(d) With an acid solution of potassium iodide, the anilide is reproduced and iodine liberated.

$$R \cdot CO \cdot NR'Cl + 2HI = R \cdot CO \cdot NR'H + HCl + I_2$$

(e) With alkaline hydrogen peroxide, oxygen is liberated and the anilide reformed.

$$R \cdot CO \cdot NR'Cl + H_2O_2 = R \cdot CO \cdot NR'H + HCl + O_2.$$

When warmed with various anilines, a vigorous reaction takes place, and the anilide is regenerated, whilst a chlorine substitution product of the aniline is formed.

These compounds all undergo a remarkable isomeric change. When an unsubstituted phenyl residue is attached to the nitrogen, the

chlorine atom associated with the latter is transferred to the ring in the para-position relatively to the substituted amido-group; a change which was first observed by Bender in the case of phenyl acetyl nitrogen chloride. When the para-position is occupied, the chlorine is transferred to the ortho-position, and when both the para- and one ortho-position are occupied, to the remaining ortho-position. The behaviour of these substituted nitrogen chlorides resembles, in this respect, that of the substituted nitramines and sulphamates (compare Bamberger, Ber., 1894, 27, 359; 1895, 28, 399; 1897, 30, 1248, 2247). In these transformations of the phenyl acyl nitrogen chlorides, however, we have never, so far, observed the simultaneous formation of ortho- and para-compounds. The latter are formed when possible to the exclusion of the former.

From the existence and behaviour of these compounds, it seems certain that, in the chlorination of anilides or anilines, the halogen first replaces a hydrogen atom of the NH- or NH₂-group, the nitrogen chloride thus formed becoming subsequently transformed into an isomeric substituted anilide or aniline. The series of changes which takes place when an anilide is chlorinated may be illustrated by the following formulæ, further chlorination proceeding on similar lines with the production, although less readily, of the 2:4:6-trichloroanilide (p. 1052).

The study of these compounds affords, we believe, an explanation of many well-known facts. In the chlorination of anilides and anilines, not only is the substitution unusually easy, but the entering halogen atom always takes up a position in the nucleus para- or orthorelatively to the NH- or NH₂-group, provided these positions are unoccupied, other substituting groups which may be present having apparently no directing influence. If, as we believe, the action of chlorine or a chlorinating agent on an anilide and probably on an aniline leads to the production of a nitrogen chloride which then undergoes isomeric change, the position taken up by the halogen in the nucleus depends chiefly on the relation of the nitrogen atom to the carbon atoms of the ring, whilst other groups present have no opportunity of exerting any specific orientating influence.

It is possible that in every case an addition of hypochlorous acid to the amide precedes the formation of these nitrogen chlorides, and our work on nitrogen iodide, which proves that the latter is formed from ammonium hypoiodite, supports this view. We have not, however, so far observed any indication of the existence of such compounds.

We have prepared substituted nitrogen bromides which undergo exactly similar intramolecular transformations, and show that bromination is effected in an exactly analogous manner.

Phenyl Formyl Nitrogen Chloride, C₆H₅·NCl·CHO.

This substance is best prepared by adding the calculated quantity of a solution of bleaching powder to a saturated solution of formanilide containing an excess of potassium bicarbonate, or to formanilide suspended in a solution of the bicarbonate. It separates as an oil which slowly solidifies, and calcium carbonate is at the same time The bleaching powder solution is run in very slowly, the mixture being vigorously stirred by the aid of a turbine; after the addition, stirring is continued for an hour or so to ensure complete conversion of the anilide into the chloride. The solid is then filtered off, and the phenyl formyl nitrogen chloride extracted by chloroform. This solution must be rapidly evaporated by a blast of air, as the impure nitrogen chloride very quickly changes into parachloroformanilide if the solvent is distilled off or allowed to volatilise. The reddishcrystalline mass which separates from the chloroform is purified by recrystallisation from a mixture of chloroform and light petroleum. It is thus obtained in long, lustrous prisms terminated by pyramids. The melting point is 47°.

0.1984 gave 0.1790 AgCi. Cl = 22.89. CrHsNOCl requires Cl = 22.83 persont.

It is very soluble in chloroform, carbon bisulphide, and benzene, but only sparingly so in light petroleum. It gives all the characteristic reactions of the nitrogen chlorides with hydrochloric acid, a solution of potassium iodide, and an alkaline solution of hydrogen peroxide, whilst with alcohol, formanilide is regenerated. On keeping for a few days, it shows signs of decomposition, developing a chlorous smell and becoming coloured. In a short time, a considerable portion is found to have changed into parachloroformanilide. This change takes place very rapidly if the substance is warmed; great heat is developed, and the action may become violent if more than a small quantity is employed. This transformation takes place quietly when the chloride is warmed under water at about 50°; the transparent oil appears to boil, and considerable heat is developed. The darker oil which is formed solidifies, as the water cools, to a mass of crystals of parachloroformanilide (m. p. 102°), which is quite pure after crystallising once from water. The yield is quantitative.

Parachlorophenyl Formyl Nitrogen Chloride, C6H4Cl·NCl·CHO.

This chloride is prepared and purified in a manner exactly similar to that used in the case of the preceding substance. It crystallises well in long, colourless prisms terminated by pyramids, melts at 95—96°, and has all the general characteristics of the group. On keeping, it soon becomes slightly pink, and slowly changes at the ordinary temperature into 2:4-dichloroformanilide. On heating at 200—210° for a few minutes, it is completely and quietly converted into the dichloroformanilide.

0.1954 gave 0.2950 AgCl. Cl = 37.33. $C_7H_8NOCl_9$ requires Cl = 37.37 per cent.

2: 4-Dichlorophenyl Formyl Nitrogen Chloride, C.H. Cl. NCl·CHO.

Formanilide can be directly converted into this compound by adding a solution in acetic acid to a large excess of a solution of bleaching powder and finally heating on the water-bath. The oil thus obtained is difficult to purify, as it generally contains a little unchanged parachlorophenyl formyl nitrogen chloride. It is preferable therefore to start with 2:4-dichloroformanilide. A solution of the latter in acetic acid is added to an excess of a solution of bleaching powder, and the mixture heated and thoroughly shaken until the oil which separates becomes transparent. The chloride solidifies on cooling, and is recrystallised from a mixture of chloroform and light petroleum. It forms thick, colourless, glistening plates melting at 44°.

0.2018 gave 0.3846 AgCl. Cl = 47.12. $C_7H_4NOCl_8$ requires Cl = 47.44 per cent.

Although this chloride develops a marked chlorous smell on keeping, decomposition takes place only to a very small extent. On heating, no sudden change occurs, but at about 200° chlorine is evolved, and the residue consists chiefly of 2:4-dichloroformanilide.

Phenyl Acetyl Nitrogen Chloride (Acetochloranilide), C₆H₅·NCl·CO·CH₂.

This compound was first obtained by Bender (los. cit.), who prepared it by adding bleaching powder to a saturated solution of acetanilide in water acidified with acetic acid. This method is unsatisfactory, as it is very difficult to obtain the nitrogen chloride in quantity, and as the slightest excess of acetic acid causes the complete conversion of

* Castoro (Gazzetta, 1898, 28, ii, 312) recently failed to confirm Bender's observations.

the substance into parachloracetanilide. It is, however, very easily and rapidly prepared by the action of bleaching powder on acetanilide suspended in excess of a solution of potassium bicarbonate. The chloride is extracted with chloroform, and recrystallised from a mixture of chloroform and light petroleum. The yield amounts to 96 per cent. of the theoretical. It crystallises in large, transparent, apparently rectangular plates, not in needles as stated by Bender, and melts at 91°. It dissolves readily in dilute acetic acid, long needles of parachloracetanilide separating as the liquid cools. This conversion also takes place slowly on keeping, being nearly complete in 2 or 3 weeks.

On treatment with hydriodic acid, a reaction occurs analogous to that which we have observed in the case of nitrogen iodide; one atom of halogen attached to nitrogen, in this case the whole of the halogen, liberates two atoms of iodine in accordance with the equation given on p. 1047. This reaction is characteristic of the nitrogen halogen linking. The determination of the iodine liberated is readily effected by dissolving the substance in chloroform, and shaking with a solution of potassium iodide acidified with acetic acid.

0.3952 liberated I = 46.02 c.c. N/10 iodine. Cl, as :NCl, = 20.64. $C_6H_5\cdot NCl\cdot CO\cdot CH_3$ requires Cl, as :NCl, = 20.9 per cent.

Parachlorophenyl Acetyl Nitrogen Chloride, C₆H₄Cl·NCl·CO·CH₃.

This substance is prepared from parachloracetanilide in the manner described above. In crystalline form, it resembles the phenyl acetyl nitrogen chloride very closely, and possesses all the general characters of the group. The melting point is 82°.

0.1942 gave 0.2718 AgCl. Cl = 34.61. $C_8H_7NOCl_2$ requires Cl = 34.76 per cent.

The estimation of chlorine attached to nitrogen gave the following results:

0.4426 liberated I = 42.9 c.c. N/10 iodine. Cl, as :NCl, = 17.18. $C_6H_4Cl\cdot NCl\cdot CO\cdot CH_8$ requires Cl, as :NCl, = 17.38 per cent.

At 165°, transformation into 2:4-dichloracetanilide takes place almost explosively. This change occurs quietly and quantitatively when the substance is heated under water. It first melts, and, when the water begins to boil, becomes converted into its isomeride with considerable evolution of heat and apparent ebullition of the oil, which afterwards solidifies.

2: 4-Dichlorophenyl Acetyl Nitrogen Chloride, CoH3Cl2 NCl CO CH3.

This substance can be prepared either directly from acetanilide, or, better, from 2:4-dichloracetanilide. The solution of acetanilide in acetic acid is poured into a large excess of a solution of bleaching powder; the precipitated anilide gradually clots together as the action proceeds, and finally, when the mixture is warmed on the water-bath, forms a clear, yellow oil which often solidifies on cooling to a hard mass of the impure chloride. To remove 2:4-dichloracetanilide, and more especially parachlorophenyl acetyl nitrogen chloride, which are probably present as impurities, the product is redissolved in acetic acid and again poured into a solution of bleaching powder, the mixture being warmed; it is then recrystallised from a mixture of chloroform and light petroleum. It is simpler to pour a solution of the pure 2:4-dichloracetanilide in acetic acid into excess of bleaching powder and apply heat. The oil which separates is shaken with a warm acid solution of bleaching powder to complete the conversion of the anilide; it solidifies when cooled, and is finally purified by recrystallising from a mixture of chloroform and light petroleum. It melts at 78°. The yield is quantitative.

2:4-Dichlorophenyl acetyl nitrogen chloride resembles the two preceding nitrogen chlorides very closely in appearance, properties, and behaviour towards reagents; it is, however, more stable, and can be kept practically unchanged for months. It is decomposed, but very gradually, by heating under boiling water. Its solution in acetic acid evolves chlorine slowly when heated, but many hours boiling are required before it is completely converted into 2:4-dichloracetanilide. In a sealed tube, a nearly quantitative yield of 2:4:6-trichloracetanilide is obtained after 4 hours heating with acetic acid at 145°: Heated alone, it decomposes at 200°, evolving chlorine and forming a dark, coloured mass, consisting largely of 2:4-dichloracetanilide.

This compound has been carefully analysed and studied, as it appears to be the main constituent of a substance obtained by Witt (Ber., 1875, 8, 1226) by the action, at 80°, of excess of bleaching powder solution on a solution of acetanide in acetic acid. The oil thus formed could not be solidified, and was regarded as an additive product of hypochlorous acid and 2:4-dichloracetanilide, $C_6H_8Cl_2\cdot NH\cdot CO\cdot CH_3+HOCl$. His analyses agree only approximately with this formula; for example, the carbon is 5 per cent. too high, and great difficulty was experienced in the combustion owing to a burst of chlorine which occurs when the substance is first heated, a peculiarity also observed by us in the case of the nitrogen chloride. We estimated the carbon and hydrogen quite easily when the substance

was mixed with a long layer of lead chromate, with the following results:

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0.2194 gave 0.3238 CO<sub>2</sub> and 0.0515 H<sub>2</sub>O. C = 40.23; H = 2.63. 0.3452 ,, 17.2 c.c. nitrogen at 13° and 756 mm. N = 5.86. 0.1606 ,, 0.2906 AgCl. Cl = 44.75. 0.516 liberated I = 43.7 c.c. N/10 iodine. Cl, as :NCl, = 14.88. C<sub>8</sub>H<sub>7</sub>NOCl<sub>3</sub> requires C = 40.26; H = 2.54; N = 5.88; Cl = 44.65; Cl, as :NCl, = 15.02 per cent.
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Two determinations of the molecular weight by Raoult's method were made, using 10 grams of benzene as solvent.

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0.2010 lowered the freezing point 0.42°. M. wt. = 234.5. 0.6442 ,, ,, 1.295^{\circ}. M. wt. = 243.7. C_8H_7NOCl_8 requires a molecular weight of 238.45.
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The behaviour of Witts's oil is identical in every respect with that of our crystalline 2:4-dichlorophenyl acetyl nitrogen chloride. When prepared by his method, it frequently solidifies with the greatest difficulty, owing to the presence of impurity, probably parachlorophenyl acetyl nitrogen chloride, which can only be removed by the treatment described above.

Phenyl Benzoyl Nitrogen Chloride, C. H. NCI·CO·C. H.

This substance is prepared by the general method from benzanilide and bleaching powder in the presence of potassium bicarbonate, but the reaction takes place less readily than with the formyl and acetyl compounds. It crystallises in colourless plates from a mixture of chloroform and light petroleum, and melts at 77°.

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0.2014 gave 0.1228 AgCl. Cl = 15.08.

C_{18}H_{10}NOCl requires Cl = 15.33 per cent.
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On heating the melted chloride to 120—130°, benzoyl chloride is given off, whilst a portion is converted into parachlorobenzanilide. The latter change is brought about quantitatively if the nitrogen chloride is heated under water for some time.

Parachlorophenyl Benzoyl Nitrogen Chloride.

We have not succeeded in obtaining this substance pure, as parachlorobenzanilide is not attacked at the ordinary temperature by hypochlorous acid. At 70—80°, either in the presence of potassium bicarbonate or acetic acid, a reaction takes place, but at this temperature the chloride becomes partly converted into 2:4-dichlorobenzanilide, which in turn forms, with the hypochlorous acid, 2:4-dichlorobenzanilide, which in turn forms, with the hypochlorous acid, 2:4-dichlorobenzanilide, which in turn forms, with the hypochlorous acid, 2:4-dichlorobenzanilide, which in turn forms, with the hypochlorous acid.

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phenyl benzoyl nitrogen chloride. On extracting the product with chloroform, an oil is obtained which solidifies only with great difficulty. Analysis of the recrystallised product showed that it consisted of about 30 per cent. of parachlorophenyl benzoyl nitrogen chloride, together with 70 per cent. of 2:4-dichlorophenyl benzoyl nitrogen chloride.

2:4-Dichlorophenyl Benzoyl Nitrogen Chloride, C6H5Cl2·NCl·CO·C6H5.

This compound, like the corresponding formyl and acetyl derivatives, can either be obtained directly from benzanilide or from 2:4-dichlorobenzanilide, by the action of bleaching powder in the presence of acetic acid at a temperature of from 80—90°. It resembles other members of the group in appearance and properties, and melts at 86°. On heating at 150—200°, benzoyl chloride is evolved and a tarry mass is left from which 2:4-dichlorobenzanilide can be isolated.

0.2096 gave 0.2992 AgCl. Cl = 35.3. $C_{18}H_8NOCl_8$ requires Cl = 35.44 per cent.

We have obtained similar compounds from many other substituted anilides, from secondary amines, and from other substances in which hydrogen is attached to nitrogen, and we desire to reserve the investigation of these compounds. We have also obtained substituted nitrogen bromides resembling the nitrogen chlorides very closely in properties.

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CV.—Synthetical Preparation of Glucosides.

By Hugh Ryan, M.A., 1851 Exhibition Scholar of the Queen's College, Galway.

By the action of alcohols and mercaptans on hexoses and pentoses in the presence of hydrochloric acid, Emil Fischer succeeded in preparing the glucosides of methylic, ethylic, propylic, isopropylic, amylic, and benzylic alcohols, of ethyleneglycol, glycerol, and ethyl, amyl, and benzyl mercaptans (*Ber.*, 1893, 26, 2400; 1894, 27, 674, 2483, 2985).

Similarly, Emil Fischer and Jennings obtained amorphous condensation products by the action of resorcinol, pyrogallol, and orcinol on different sugars. The method was found to be inapplicable for the preparation of glucosides of the monohydric phenols (*Ber.*, 1894, 27, 1358). Phenol and its homologues can be converted into well crystallised glucosides by Michael's method (Compt. rend., 1879, 89, 355); this, however, is troublesome, and as it gives poor results, its employment hitherto has been very limited. I sought to improve the process by employing inactive pentacetylglucose, which is more easily prepared than acetochloroglucose, but could not isolate any crystalline compound from the product of its reaction with potassium phenolate.

The best results were attained by a slight modification of Michael's method. The phenol (1 mol.) was dissolved in alcoholic potash (1 mol.) and to the clear solution was added acetochloroglucose (1 mol.) dissolved in absolute alcohol. The yield was satisfactory.

The acetochloroglucose required was prepared by Colley's method (Ann. Chim. Phys., 1870, [iv], 21, 363), with some slight alterations which render it more easily accessible. Pure, crystallised, anhydrous glucose (18 grams), after passage through a fine sieve, was mixed with acetyl chloride (39 grams) in a well-dried Volhard tube; this was sealed off at once and shaken during 24-30 hours at the ordinary temperature. The colourless solution was dissolved in chloroform, and shaken with ice cold sodium carbonate. The chloroform solution was filtered, dried with calcium chloride, and, after evaporation in a vacuum, gave a colourless, semi-solid mass of acetochloroglucose. It may be mentioned that attempts to prepare acetochloroglucose in an open vessel protected from atmospheric moisture by a calcium chloride tube were unsuccessful. When 20 mols, of acetyl chloride were employed with 1 mol. of glucose, the principal product was the dextrorotatory pentacetylglucose previously made by Erwig and Königs by the action of acetic anhydride and zinc chloride on grape-sugar (Ber., 1889, 22, 1464). It melted at 110°, and on analysis gave the following result:

0.1389 gave 0.2490 CO₂ and 0.0717 H₂O. C = 48.9; H = 5.7. $C_{16}H_{22}O_{11}$ requires C = 49.2; H = 5.6 per cent.

β-Naphthylghucoside, C₆H₁₁O₅·O·C₁₀H₇.—A solution of acetochloroglucose (70 grams) in absolute alcohol (150 c.c.) was added to β-naphthol (28 grams) and potassium hydroxide (11 grams) dissolved in absolute alcohol, the total volume of the well-cooled mixture being about 300 c.c. After a few minutes, the solution became turbid, owing to the separation of potassium chloride. After remaining for three days at the ordinary temperature, the yellowish-brown solution, which smelt strongly of ethylic acetate, was heated to boiling for 45 minutes under a reflux condenser, cooled, and filtered. After removal of the alcohol on the water-bath, a little water was added, and the solution, on cooling, solidified. The product (46 grams), which contained some unchanged naphthol, was recrystallised from boiling water, and finally from absolute alcohol. It separated in groups of

long needles melting at 184—186°, and was dried at 105° before analysis.

0.1806 gave 0.415 CO_2 and 0.0944 H_2O . C = 62.67; H = 5.81. $C_{16}H_{18}O_6$ requires C = 62.74; H = 5.88 per cent.

β-Naphthylglucoside is soluble in alcohol or hot water, sparingly so in acetone, and almost insoluble in benzene, light petroleum, cold water, or ether. It is readily hydrolysed by dilute acids or emulsin, reduces Fehling's solution only after hydrolysis, and is stable towards dilute alkali, in which it is scarcely soluble. The taste is disagreeable.

A similar experiment with paranitrophenol did not lead to the formation of a glucoside. In order to find whether the failure of the reaction was due to the nature or position of the nitro-group, I examined the behaviour of paracresol towards acetochloroglucose, with results which show that the position of the radicle does not explain the failure in the case of nitrophenol.

Paracresylglucoside, $C_6H_{11}O_5\cdot O\cdot C_6H_4\cdot CH_3$.—Acetochloroglucose (36 grams), dissolved in absolute alcohol, was added to a solution of paracresol (11 grams) and potassium hydroxide (6 grams) in alcohol. The mixture, which became yellow, was left for 14 hours in ice water, and then at the ordinary temperature for a day. The resulting crystalline magma was diluted with absolute alcohol to 500 c.c., left for two days, and then boiled gently for $1\frac{1}{2}$ hours. The filtrate, when left in an evaporating dish for a few days, gave a separation of the glucoside in needles which were scarcely soluble in ether, benzene, light petroleum, or chloroform, sparingly so in acetone, and soluble in alcohol or water. It melted at 175—177°, after drying at 100°, and did not reduce Fehling's solution before, but readily after, hydrolysis, with emulsin or dilute acids. The yield of pure product amounted to 40 per cent. of the theoretical.

0.1737 gave 0.3652 CO₂ and 0.1045 H_2O . C = 57.34; H = 6.74. $C_{18}H_{18}O_6$ requires C = 57.77; H = 6.66 per cent.

Orthocresylglucoside, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_3$, was prepared from orthocresol in a similar manner. It crystallised from water in beautiful needles, melted at $163-165^\circ$, was scarcely soluble in ether but easily so in water or alcohol, and did not reduce Fehling's solution before, but readily after, hydrolysis by dilute acids or emulsin. It had an intensely bitter taste. The yield was similar in amount to that obtained from the para-derivative. The crystals were dried at $105-110^\circ$ before analysis.

0.1406 gave 0.2966 CO₂ and 0.0894 H₂O. C = 57.53; H = 7.06. $C_{18}H_{18}O_6$ requires C = 57.77; H = 6.66 per cent.

 $Carvacrylglucoside, \textbf{C}_{6}\textbf{H}_{11}\textbf{O}_{5} \cdot \textbf{O} \cdot \textbf{C}_{6}\textbf{H}_{8}(\textbf{CH}_{8}) \cdot \textbf{C}_{3}\textbf{H}_{7} + \tfrac{1}{2}\textbf{H}_{2}\textbf{O}, \text{was prepared}$

from carvacrol in a similar manner. A yellowish, oily residue was obtained by the spontaneous evaporation of the filtrate from the potassium chloride formed in the reaction; this was evaporated with water several times on the water-bath until the odour of carvacrol disappeared, and afterwards crystallised from hot water. It separates in groups of beautiful needles, and when anhydrous softens at 118° and melts not quite sharply at 135°.

The glucoside, after drying over calcium chloride, but not in a vacuum, was analysed.

0.1806 gave 0.3964 CO₂ and 0.1279 H₂O. C = 59.8; H = 7.9.

0.2384 lost 0.0064 H_2O at 90° in a vacuum over phosphorus pentoxide. $H_2O=2.7$.

 $C_{16}H_{24}O_6 + \frac{1}{2}H_2O$ requires C = 59.8; H = 7.8; $H_2O = 2.8$ per cent.

The anhydrous compound gave the following numbers:

0.1512 gave 0.3392 CO₂ and 0.1086 H₂O. C = 61.2; H = 7.9. $C_{16}H_{24}O_6$ requires C = 61.5; H = 7.7 per cent.

Carvacrylglucoside is easily soluble in alcohol or acetone but less readily so in cold water or ether, and is almost insoluble in benzene, chloroform, or light petroleum. It does not reduce Fehling's solution before, but readily after, heating with emulsin or dilute mineral acids.

The behaviour of carvacrylglucoside towards dilute aqueous alkali is characteristic. Just as if it retained an unchanged phenolic hydroxyl group, it dissolves slowly, but completely, in dilute caustic soda. That its solubility is not due to decomposition of the glucoside into its components by the action of the alkali is shown by the fact that it scarcely reduces Fehling's solution even after prolonged boiling.

Similar properties seem to be possessed by a galactoside obtained from β -naphthol and acetochlorogalactose, the latter substance having been prepared by the action of acetyl chloride on galactose.

As glucosides of the type $C_6H_{11}O_5$ ·R·OH, to which carvacrylglucoside and naphthylgalactoside apparently belong, are unknown, the investigation of these substances will be continued. Attempts to prepare glucovanillin and menthylglucoside have not been up to the present successful. Similar experiments will be made with anthranol and alizarin.

It is noteworthy that all the glucosides hitherto prepared from acetochloroglucose in alkaline solution are readily hydrolysed by emulsin.

My best thanks are due to Professor Emil Fischer for his advice during the course of this investigation.

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CVI.—The Action of Sulphuric Acid on Fenchone.

By JAMES E. MARSH.

If fenchone is warmed with strong sulphuric acid, sulphur dioxide is given off and acetoxylene [Me: Me: Ac = 1:2:4] is formed. This compound has been obtained synthetically by Claus by the action of acetyl chloride on orthoxylene in presence of aluminium chloride (J. pr. Chem., 1890, [ii], 41, 396). Armstrong and Kipping (Trans., 1893, 63, 75) obtained the same compound by the action of sulphuric acid on camphor; they found that camphor is not readily acted on by sulphuric acid at a temperature below 100°, that it was most advantageous to heat the mixture to 110°, that acetoxylene is not the only product of the reaction, and that it was not practicable to separate the compound in a pure state by fractional distillation; they effected its separation by preparing the crystalline phenylhydrazone from it and decomposing this by hydrolysis.

When fenchone was warmed with five times its volume of strong sulphuric acid, the action began at a temperature below 50° with evolution of sulphur dioxide. The evolution of gas was rapid at 80°, and at 100° was complete in a few minutes. I used small quantities of not more than 10 c.c. of fenchone in one operation. It appeared preferable to keep the temperature at about 80°, and there was little or no charring. After cooling, the solution was poured into water and distilled in steam. The distillate was shaken out with ether and the ethereal solution distilled under reduced pressure. After the ether and water had come off without condensing, the residue distilled almost entirely at 131° under 20 mm. pressure; it amounted to about 70 per cent. of the fenchone taken. If we take into consideration the loss arising from the number of operations which the fenchone had undergone, and that only 10 grams were used, the yield of acetoxylene probably approximates to that required by theory. It was redistilled and the fraction boiling at 131° under 20 mm. pressure was analysed. It gave

C = 80.6; H = 8.3. $C_{10}H_{12}O$ requires C = 81.0; H = 8.1 per cent.

The acetoxylene so obtained was a nearly colourless oil smelling somewhat of cinnamon. Its specific gravity was found to be 0.9968 at 20°/4°. When treated with hydroxylamine hydrochloride and caustic potash in alcoholic solution, it gave a good yield of the oxime which crystallised from methylic alcohol, forming colourless crystals melting at 86—87°. Claus gives the melting point at 88—89°, Armstrong and Kipping at 84.5—85.5°.

To further establish its identity and constitution, a small quantity

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was oxidised by warming gently with a slight excess of bromine dissolved in 4 per cent. caustic soda solution, until bromine was scarcely liberated by addition of acid. On filtering from the crystals of carbon tetrabromide, and on addition of dilute sulphuric acid, a thick precipitate was thrown down which, after crystallising from dilute alcohol, melted at 163°. On analysis the product gave

C = 71.6; H = 6.7. $C_9H_{10}O_9$ requires C = 72.0; H = 6.6 per cent.

The silver salt was prepared and, on analysis, gave

Ag = 41.8. $C_6H_8Me_2 \cdot COOAg$ requires Ag = 42.0 per cent.

The acid thus obtained by oxidation of acetoxylene is paraxylic acid $[CH_3: CH_3: COOH = 1:2:4]$.

It seems reasonable to suppose that the almost quantitative conversion of fenchone into acetoxylene ought to have an important bearing on the constitution of fenchone. I have attempted in a paper on "The Constitution of Camphor" (*Trans. Oxford Univ. Jun. Sci. Club N.S.*, 1898,110) to show how the formation of acetoxylene from camphor, established by Armstrong and Kipping, may be explained; I here only wish to point out that fenchone is probably still more nearly related in constitution to acetoxylene than is camphor, judging from the ease with which this compound is obtained from fenchone compared with the difficulty of its production from camphor. The following formula for fenchone was put forward last year by Wallach (*Annalen*, 1898, 300, 320) and by Gardner and Cockburn (Trans., 1898, 73, 708) independently:

$$\begin{array}{c|c} \operatorname{CH}_2 \cdot \operatorname{CH} & \longrightarrow \operatorname{CH} \cdot \operatorname{CH}_3 \\ & \operatorname{C}(\operatorname{CH}_3)_2 \\ & \operatorname{CH}_2 \cdot \operatorname{CH} & \longrightarrow \operatorname{CO} \end{array}$$

The coincidence of two separate lines of research leading to the same conclusion might be regarded as affording at least a presumption in favour of the formula. But the coincidence is less remarkable seeing that the formula is constructed on the model of Bredt's camphor formula. Further, neither Wallach nor Gardner and Cockburn express themselves as satisfied with the formula, and bring forward objections to it which seem to me not less convincing than their arguments in its favour. To these objections I think ought to be added the formation from fenchone of acetoxylene which it seems impossible to reconcile with the formula proposed.

I have from time to time ventured to criticise some of the formulæ proposed for members of the terpene group, partly on the ground that they do not account for the derivatives of benzene which are obtained from them by comparatively simple reactions. Nor does it seem to

me obvious why it should be regarded a sounder principle to base the constitution of closed chain compounds, such as the terpenes, on the products obtained by breaking down their cyclic structure, than on those products in which a ring remains. At present there seems to be an inclination either to disregard the latter entirely, or in certain cases to make a selection of those benzene derivatives which may be accounted for. It is not unreasonable to require that any constitution assigned to a member of the terpene group must account for both the aromatic and the fatty derivatives obtained from it.

I wish to thank Mr. Gardner and Mr. Cockburn for kindly giving me the samples of fenchone with which these experiments were made.

University Museum,
Oxford.

CVII.—On a Method for Providing a Current of Gaseous Chloroform mixed with Air in any desired proportion, and on Methods for Estimating the Gaseous Chloroform in the Mixtures.

By A. VERNON HARCOURT, M.A., F.R.S., Lee's Reader in Chemistry at Christ Church, Oxford.

When air is passed through a mixture of alcohol and chloroform, both liquids evaporate, and if the surface of contact of the air bubbles and the liquid is sufficiently extensive relatively to the total volume of air passed through, the maximum tension is reached of each vapour as given off from the actual mixture of the two at the actual temperature. From the mixed gases, the vapour of alcohol may be withdrawn by passing them through sulphuric acid, the gases which go forward being a mixture of air and chloroform in proportions dependent upon the proportion of alcohol to chloroform in the mixed liquid and upon the temperature of the liquid, which must not exceed that of the air around.

Since the density of alcohol is much less than that of chloroform, mixtures of the two liquids in different proportions differ much in density, and the composition of a mixture can be adjusted and kept constant by bringing it to a known density by additions of either alcohol or chloroform.

The method, resting upon these facts, which is here proposed consists in leading dry air through a bent tube to the bottom of a Wolfe's bottle, which is half filled with glass balls and charged with a mixture of alcohol and chloroform, and thence through two washing vessels containing respectively sulphuric acid and water. The air issuing from a number of small holes made in the lower branch of the

tube passes up by many channels among the glass balls into the liquid With a bottle of about 1200 c.c. capacity, this contact is sufficient to saturate air passing at the rate of at least 1 cubic foot per hour, as has been proved by analysing the gaseous mixture when produced at that rate, and with air passing at the rate of 1 cubic foot per hour, and finding that the composition was the same.

The density of the liquid can be conveniently observed while the air is passing by means of two small bulbs, one of which floats and the other sinks when the liquid has the desired density. operation proceeds, the proportion of chloroform diminishes, and more is added until the lighter bulb again comes to the surface.

In order to ascertain what was the proportion of chloroform vapour mixed with air which had given satisfactory results as an anæsthetic. two methods were tried.

I. The first method depends upon the action on chloroform of an alcoholic solution of caustic potash, which produces potassium formate and potassium chloride,

$$CHCl_3 + 4KHO = 3KCl + H \cdot COOK + 2H_2O.$$

This reaction takes place slowly, and is, perhaps, accompanied to a small extent by some other reaction, leaving other products. Even when an alcoholic solution of potash is heated with a small amount of chloroform to a temperature of 50-70° for some hours, the chloride formed does not correspond to the whole of the chloroform; and, consequently, quantitative estimations of chloroform depending upon this reaction yield results which are a few per cent. too low. Under constant conditions, however, the deficiency is nearly constant, and thus, by applying a correction, results are obtained which may be sufficiently accurate for the object in view.

For bringing about the requisite contact between the alcoholic potash and the mixture of chloroform and air, either the mixed gases may be led slowly through the alcoholic solution, or they may be collected in a bottle or flask and there treated with the reagent. short account may be given of the way in which each of these modes of testing was conducted. For the first, the air and chloroform were passed through a long and almost horizontal tube, the upper surface of which had been pressed in at intervals of a few centimetres, so that while the solution with which it was charged moved about freely, the bubbles of gas were arrested at successive stages. A lamp placed beneath the tube, near its inlet, heated every portion of the liquid in turn to a temperature at which the chloroform vapour which has been dissolved undergoes the above change, while the air about to escape at the opposite end gave up the last portions of chloroform to alcohol which had been freed from the chloroform already absorbed and was

of a lower temperature. When the first part of the experiment was complete, the liquid was neutralised with dilute nitric acid, and in a portion of it the mass of chlorine, and thus the mass of chloroform, was measured by adding to it in a porcelain dish two drops of a solution of potassium chromate and a standard solution of silver nitrate from a burette.

In experiments made with a view to test the method, air was driven by a water-pump through a small meter, and thence through the vessel in which it was mixed, under the conditions to be tested, with the vapour from a known weight of chloroform, and thence through the washing-tube in which the chloroform was arrested and decomposed.

Some of the results obtained by this method were as follows:

Weight of Chloroform.

Taken.		Found.	Found per cent.
0.236		0.219	93
0.226	•	0.212	94
0.212		0.197	93
0.225		0.218	97
0.179		0.175	98
0.140		0.135	96

In the course of these successive experiments, as the results fell too low, various further precautions were taken, such as avoiding contact between chloroform vapour and india-rubber, which has an absorbent action. But the deficiency could only be reduced from 6 or 7 to 3 or 4 per cent.

A plan, which led up to the method already described for making a mixture of air with chloroform suitable for anæsthetic purposes, was tested by this method. Mixtures of chloroform and alcohol were brought into a tube similar to that which held the alcoholic potash, and the measured volume of air was passed through the two, bubble by bubble. In the following table, the volume of chloroform vapour found has been increased by 4 per cent.:

Relative masses of alco		Temperature.	Vol. of chloroform vapour in 100 vols. of air	
Chloroform.	Alcohol.	-	and chloroform.	
20 30	80 70	15°	2·35 2·20 4·28 4·27	

Since in the use of chloroform as an anæsthetic air must be charged with the vapour at a far greater rate than that of the foregoing experiments, some bottles were filled with the mixture made in the manner described on p. 1060, and their contents were displaced by water, and so gradually driven through the heated solution of potash in alcohol. But as in this method the chloroform vapour is exposed to the action of a large volume of water in which, even at a low tension, it is to some extent soluble, and the substitution of mercury on the same scale would be inconvenient, the second mode of testing was tried, that of bringing a measure of alcoholic potash into the bottle in which the chloroform and air had been collected, pressing and tying in the stopper of the bottle, and heating the contents.

Control experiments were first made, in which a weighed amount of chloroform was brought into the bottle in a bulb which was broken before the measure of alcoholic potash was introduced. As the volume of gas within the bottle is increased by the amount of the chloroform vapour formed from the liquid, room was made for this amount by heating the bottle, whose sides were wet, before the stopper was put in and the bulb broken. Thus, when the bottle which had cooled was opened to bring in the alcoholic potash, the internal gaseous pressure was not in excess of the atmosphere pressure, and the only loss was that, allowed for in the calculation, of a portion of the contained gases equal to that of the liquid brought in. In some cases, the precaution was taken of sealing up the alcoholic potash in a tube of thin glass, so that no contact should occur till the stopper had been securely fixed in the neck of the bottle. To charge the bottles, whose capacity had been measured, many times their volume of the mixture of chloroform and air to be analysed was passed through them.

In order to complete the reaction as far as possible, the bottles were immersed one-quarter in a water-bath, of which the temperature was gradually raised to about 60° and kept at this point for several hours. The liquid contents were then poured and washed out, and the amount of potassium chloride formed was determined with a standard solution of silver nitrate. The results thus obtained agree with those already given, as will be seen from the following tables:

Weight of Chloroform.

Taken.	Found.	Found per cent.
0.032	0.031	97
0.0156	0.0144	92
0.0378	0.0359	95
0.037	0.0344	93
0.056	0.054	96
0.0837	0.0801	96

The deficiency, in spite of all the precautions which repetitions of the experiment suggested, again amounts to 4 or 5 per cent. Accordingly, the percentage of chloroform in mixtures of air and chloroform, prepared by the method described on p. 1060 and analysed by this method, have in the following table been increased by 4 per cent.:

Relative masses o		Temperature.	Vol. of chloroform vapour in 100 vols. of
Chloroform.	Alcohol.		mixed gases.
30	70	15°	4.45
,,	,,	,,	4.37
,,	,,	"	4.03
. ,,	,,	,,,	4 ·21 4 ·28
,,	**	' "	1 20

The differences in the above results are mainly actual differences in the mixtures analysed. The probable error of the analysis does not exceed about 2 per cent., but this is rather large, and no method involving an empirical correction can be regarded as satisfactory. Consequently, a better method was sought for, and, after various experiments which need not be related, was found.

II. The second method depends upon the reaction between chloroform vapour, air, and steam, in contact with a red-hot platinum wire. The final result of the reaction is expressed by the equation,

$$2CHCl_3 + 2H_2O + O_3 = 2CO_2 + 6HCl.$$

The probable order of the reaction is that the chloroform molecules with air around them as they fly against the heated wire are burnt, like moths in a candle, and that the chlorine thus produced reacts similarly with the molecules of steam forming hydrogen chloride and oxygen. The reverse action of hydrogen chloride and oxygen one upon another also takes place, but to an extent which, if the requisite conditions are observed, is ultimately insignificant, in consequence of the almost complete withdrawal of hydrogen chloride from the gaseous system by the water which is present. When the reaction is complete, the amount of hydrogen chloride which has been formed is determined. This may be done by means of a standard solution of silver nitrate, or equally well by means of a standard solution of ammonia.

The conditions which must be observed in order that all the chlorine atoms in the molecules of chloroform may pass into molecules of hydrogen chloride are as follows:

(1.) The proportion of steam to oxygen must be sufficiently large.

Experiments were made in which oxygen was used instead of air, and in which the water in the bottle was not heated. In both cases, the gas within the bottle when it was opened smelt of chlorine, and the results were too low.

(2.) The platinum wire must be heated to bright redness.

In experiments in which the wire was kept faintly red, the gas smelt of chlorine and the results were many per cent. too low.

(3.) The conditions of the change must be maintained for a sufficient time. If the wire is very bright, the change is complete in half an hour, but it is better not to run any risk of fusing the platinum wire, and to allow one hour for the completion of the change.

The method finally adopted is as follows. Pass the mixture of air and chloroform to be analysed into a round 1-litre flask holding about 4 c.c. of water, so that the gas, delivered near the bottom, will escape near the top, and continue the passage of the gas till five or six times the volume which the flask contains has passed through it. Substitute for the cork and tubes used in charging the flask a cork with two tubes, into which stout platinum wires have been fused, which are joined by a loop of thin platinum wire. The tubes and stout wires are of such a length that the lowest part of the loop descends to near the bottom of the flask. When the cork carrying these tubes has been pressed and tied into the neck of the flask, a little mercury is brought into each tube and copper wires are passed down the tubes; through these wires an electric current is passed sufficient to heat the loop of platinum wire to bright redness. The flask is supported in a shallow dish holding a little water, whose temperature is kept between 50° and 60°. After remaining thus for an hour, the flask is allowed to cool, and more water is brought in little by little and shaken up with the contents. Finally, the amount of dilute hydrogen chloride which has been formed is determined in the flask itself by means of a standard solution of ammonia.

The results of the test experiments made with weighed quantities of chloroform are given in the following table:

Weight of Chloreform.

Taken.	Found.	Found per cent.
0.0641	0.0638	99.4
0.0726	0.0735	101.3
0.0882	0.0879	99.7
0.0845	0.0838	$\mathbf{99 \cdot 2}$
0.0803	0.0800	99.6

This method has been applied in the analysis of mixtures of gaseous chloroform and air, prepared by the method described on p. 1060.

The following is the composition of some of the mixtures of air and chloroform vapour thus produced from mixtures of alcohol and chloroform in different proportions, and in one case at different temperatures:

Relative masses of chloroform and alcohol.		Temperature.	Vol. of chloroform	
Chloroform. Alcohol.	•	vapour in 100 vols.		
20 \$0 40 50 60 80 30	80 70 60 50 40 70 70	15° ,, ,, ,, 12 14 18	2·34 4·23 5·16 7:17 9·85 4·06 4·10 4·65	

The work here recorded was done in the Laboratory of Christ Church, Oxford, with the assistance of Mr. G. W. F. Holroyd, to whose skill and perseverance the author is greatly indebted.

CVIII.—The Application of Powerful Optically Active Acids to the Resolution of Externally Compensated Basic Substances. Resolution of Tetrahydroquinaldine.

By William Jackson Pope and Stanley John Prachey.

In the present communication, we describe the separation of compensated tetrahydroquinaldine into its optically active components by means of Reychler's dextrocamphorsulphonic acid; we have previously discussed the reasons for using this acid in preference to tartaric acid (Trans., 1898, 73, 893). The new method adopted, which is a generally applicable one, is based upon the following considerations.

The solubilities of the salts $(dB \ dA)$ and $lB \ dA)$ of a dextrorotatory acid (dA) with a dextro- and a levo-base (dB) and (dA) would hardly be expected to differ considerably, because the solubility is partly a function of the chemical nature of the salts. If, however, the salt, (dA), is the less soluble and only sufficient of the active acid, (dA), necessary to the formation of this salt is added, the balance of acid required to dissolve the base being made up by adding the requisite amount of an optically inactive acid, such as hydrochloric acid, which forms com-

paratively soluble salts with the base, it would be expected that on crystallisation the greater part of the levo-base would separate as the sparingly soluble salt, lB dA, whilst the mother liquors would retain the dextro-base of which the hydrochloride, dB HCl, is very soluble. The disadvantage of the ordinary method of separating externally compensated bases by crystallisation with excess of tartaric acid lies very largely in the fact that the solubilities of the two salts. dB dA and lBdA. are not sufficiently different to permit of the pure salts being easily isolated by fractional crystallisation; this is illustrated by Ladenburg's observation (Ber., 1894, 27, 77) that the crude dextrotetrahydroquinaldine dextrobitartrate obtained from the inactive base must be recrystallised many times before it is obtained pure. applying our method to this base (using one molecular proportion each of dextro-a-bromocamphorsulphonic acid and of hydrochloric acid for the dissolution of two molecular proportions of externally compensated base) and crystallising the first separation twice from alcohol to remove mechanically retained impurities, a pure sample of lævotetrahydroquinaldine dextro-a-bromocamphorsulphonate is obtained.

Although the separation was best effected in this way, instructive results were obtained by modifying the method of applying the principle above explained.

Thus, hot aqueous solutions of one molecular proportion of ammonium dextro-a-bromocamphorsulphonate and of two molecular proportions of racemic tetrahydroquinaldine hydrochloride were mixed and the liquid allowed to cool; a large separation of lævotetrahydroquinaldine dextro-a-bromocamphorsulphonate was thus obtained in a practically pure condition, this being the least soluble salt which could be formed.

A further great advantage of making use of the formation of a sparingly soluble salt of a strong acid in the resolution of externally compensated bases is found in the fact that such sparingly soluble salts are not decomposed by feeble acids. Thus, a fairly serviceable method of obtaining levotetrahydroquinaldine dextro-a-bromocamphorsulphonate consists in adding an aqueous solution of one molecular proportion of ammonium dextro-a-bromocamphorsulphonate to an acetic acid solution of two molecular proportions of the externally compensated base; the solution soon affords a copious deposit of crystals of levotetrahydroquinaldine dextro-a-bromocamphorsulphonate.

I. LEVOTETRAHYDROQUINALDINE.

 $\label{eq:local_local_local} L & \textit{exvotetrahydroquinal dins. Dextro-a-bromocamphorsulphonate}, \\ C_{10}H_{13}N, C_{10}H_{14}BrO \cdot SO_{8}H.$

The most convenient method of preparing lævotetrahydroquinaldine dextro-a-bromocamphorsulphonate consists in mixing a hot con-

centrated solution of one molecular proportion of crude externally compensated tetrahydroquinaldine hydrochloride with a hot concentrated solution of one molecular proportion of the base in one molecular proportion of a concentrated dextro-a-bromocamphorsulphonic acid solution prepared as we have previously described (Trans., 1898, 75, 895). By the time the solution has cooled to the ordinary temperature, the greater part of the salt of the lævo-base has crystallised; the separation is filtered off, washed with dilute alcohol, and recrystallised from boiling absolute alcohol. After two recrystallisations, the substance is obtained as a mass of colourless needles melting at 223—225°. It is sparingly soluble in cold, and moderately so in hot alcohol or water; it is more soluble in glacial acetic acid, but nearly insoluble in acetone or ethylic acetate.

The crystals deposited as the hot alcoholic solution cools are long, flattened needles with obliquely placed end faces; the extinction in the large flat face is straight with the sides, and through this face the bisectrix of a large optic axial angle emerges nearly normally. double refraction is negative in sign and the optic axial dispersion is marked, the optic axial angle for red light being greater than that for blue; the optic axial plane is parallel to the long edges of the crystals. No goniometrical measurements could be obtained. After melting the salt on a microscope slide under a cover slip and subsequently cooling quickly, it remains amorphous, and signs of crystallisation only appear at the edges of the preparation after several days preservation at the ordinary temperature. By alternately cooling and heating the liquid film several times, crystallisation may be started, and once started proceeds rapidly at temperatures not much below the melting point; at the ordinary temperature, however, the crystallisation proceeds with extreme slowness even after it has been started at a higher temperature. The crystalline film thus obtained consists of a radiate mass of long needles which crack across the direction of growth as cooling proceeds; these needles are crystallographically identical with the crystals deposited from the alcoholic solution, and mostly show the optically negative bisectrix of a large optic axial angle emerging nearly normally to the plate.

The following analytical results were obtained:

The specific rotatory power of the salt was determined in absolute

alcohol and in glacial acetic acid solutions. A solution in glacial acetic acid of 0.5005 gram in 25.2 c.c. gave $a_0 + 1.54^{\circ}$ at 21.2° in a 200 mm. tube, whence $[a]_D + 38.8^\circ$ and $[M]_D + 177.6^\circ$. A solution in absolute alcohol of 0.2005 gram in 25.2 c.c. gave $a_D + 0.66^{\circ}$ at 21° in a 200 mm. tube, whence $\left[a\right]_{D} + 41.5^{\circ}$ and $\left[M\right]_{D} + 190^{\circ}$.

Lævotetrahydroquinaldine,

Carefully purified levotetrahydroquinaldine dextro-a-bromocamphorsulphonate is distilled in a current of steam with a slight excess of soda; the base is obtained as a colourless oil suspended in the aqueous distillate and is extracted with ether. The ethereal solution is dried with potash and the solvent distilled off; the residual pale yellow oil is then distilled under reduced pressure. It passes over as a colourless oil boiling at 158° under 59 mm. pressure, and is sparingly soluble in water, but miscible with the ordinary organic solvents; it has a faint basic odour and gradually becomes yellow on exposure to the air. The following analytical results were obtained:

0.1876 gave 0.5593 CO₂ and 0.1511 H₂O. C=81.31; H=8.95. 0.2977 , 24.6 c.c. of dry nitrogen at 21° and 761 mm. N = 9.65. $C_{10}H_{18}N$ requires C = 81.63; H = 8.84; N = 9.52 per cent.

The base has $a_D - 59.24^{\circ}$ in a 100 mm, tube at 20°; whence $[a]_D - 58.12^\circ$ and $[M]_D - 85.44^\circ$ at 20°. The relative density is 1.02365 at 14.5°/4°. Further details as to the physical properties are given in a subsequent paper (this vol., p. 1111).

Lævotetrahydroquinaldine Hydrochloride, $C_{10}H_{18}N,HCl+H_{2}O$.

A warm solution of pure lævotetrahydroquinaldine in excess of concentrated hydrochloric acid yields on cooling a large separation of the hydrochloride as a white, crystalline powder; this is filtered on the pump, washed with concentrated hydrochloric acid, in which the salt is moderately soluble, and recrystallised from absolute alcohol. melts at 196.5—197.5° and is fairly soluble in water, less so in absolute alcohol, and sparingly soluble in acetone. The following analyses of the air-dried material show it to contain 1H₂O which is lost at 100°:

0.1428 gave 0.1021 H₂O and 0.3118 CO₂. C = 59.55; H = 7.94.

0.3162 , 0.2258 AgCl. Cl = 17.66.

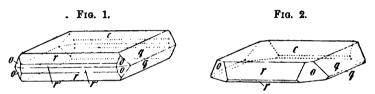
1.9828 lost 0.1765 H_0O in 4 hours at 100° . $H_2O = 8.90$.

 $C_{10}H_{18}N,HCl + H_2O$ requires C = 59.58; H = 7.94; Cl = 17.57; $H_2O = 8.93$ per cent.

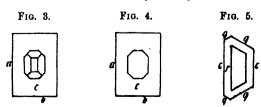
On prolonged heating at 100°, the material volatilises slowly, and Digitized by Google afterwards does not melt so sharply as before.

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The alcoholic solution, on spontaneous evaporation, deposits the hydrated salt as large, transparent, lustrous tablets belonging to the orthorhombic system (Fig. 1). The form $c\{001\}$ is dominant and gives very good results on measurement; the forms $q\{011\}$ and $r\{101\}$ are the next largest and are well developed. The pyramid $o\{561\}$ is always present and fairly large, but the dome $r'\{501\}$ is very rarely observed. There is a perfect cleavage parallel to $r\{101\}$, and the optic axial interference figure may be observed through a flake hacked parallel to $b\{010\}$. The axis-b is the acute bisectrix, and the optic axial plane is $a\{100\}$; the optic axial angle is not large, and the double refraction is fairly strong and negative in sign. The optic axial dispersion is marked, the angle for red light being greater than that for blue.



No evidence of the sphenoidal hemihedrism was obtained. The form $o\{561\}$ is never completely developed, but usually only one half of its total number of faces is present; this, however, is apparently due to the crystal growing whilst resting upon the face $c\{00\overline{1}\}$, which results in an imperfect development of those faces cutting the negative end of the c-axis. Thus the crystals very usually present the appearance shown in Fig. 2, only the four faces (561), (561), (561), and (561) of the form $o\{561\}$ being present. We were unable to obtain any evidence of enantiomorphous hemihedrism by etching; the action of water and alcohol upon the faces of the pinacoid $c\{001\}$ gives rise to etch-figures having the appearance shown in Figs. 3 and 4 respectively, whilst upon a cleavage plate parallel to $r\{101\}$ water produces etch-figures of the outline shown in Fig. 5. These figures appear to be quite in accordance with holohedral symmetry.



Crystalline System.—Orthorhombic.

a:b:c=0.8627:1:1.4124.

Forms observed.— $c\{001\}$, $q\{011\}$, $r\{101\}$, $r'\{501\}$, and $o\{561\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean observed.	Calculated.
$cq = 001:011$ $qq = 011:01\overline{1}$ $eq = 00\overline{1}:011$ $cr = 001:101$ $rr = 101:10\overline{1}$ $cr = 00\overline{1}:101$ $cr = 00\overline{1}:101$ $cr' = 001:501$ $rr' = 10\overline{1}:501$ $rr' = 10\overline{1}:501$ $qr = 011:101$ $qv = 011:561$	87 14 12 41 16 24 19 11 14 6	54°19'— 55°11' 70 8— 71 5 124 42—125 37 57 59— 59 1 62 9— 63 18 121 4—122 0 62 16— 83 25 23 54— 24 50 38 0— 39 4 72 6— 72 57 50 2— 51 8	54°42′ 70 40 125 15 58 35 62 47 121 31 82 54 24 20 38 26 72 31 50 85	70°362 125 18 ————————————————————————————————————
co = 001 : 561 $ co = 001 : 561$	15 7	84 86 — 85 41 94 40 — 95 27	85 4 94 59	85 9 94 51

After cautiously melting anhydrous levotetrahydroquinaldine hydrochloride under a cover slip on a microscope slide, it begins to crystallise quite readily at about 60°, yielding a film which is macroscopically very transparent. As the temperature falls, however, the speed of growth decreases, and at the ordinary temperature crystallisation proceeds so slowly that it cannot be followed microscopically. Further, the crystalline material obtained at temperatures not far removed from the melting point, consists of long needles or of large square plates showing straight extinction; these are striated parallel to one side and the strice are the trace of the optic axial plane, a bisectrix of positive double refraction emerging normally to the large square face. The optic axes emerge outside the microscope field, and this material is of orthorhombic crystalline form.

As the very transparent film cools, large patches of it successively change with great rapidity, becoming very white and opaque; in a thick film, the change is almost explosive in character, sometimes even throwing the cover slip into the air. Notwithstanding this, it is very improbable that the change is due to polymorphism, as, although the material becomes so opaque, yet the optical properties can still be made out and are not appreciably altered; the rupture is apparently due to strain set up during cooling. At a little below the temperature at which the hydrochloride solidifies most readily, crystallisation still proceeds, although more slowly, the same modification being produced as at higher temperatures; the crystallisation proceeds from centres just as before with production of radiate aggregates of long needles, showing well-defined extinction and optical properties. These aggregates, however, do not fly to pieces on cooling, but remain transparent, merely cracking across the longer dimensions of the needles. At the

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ordinary temperature, the substance crystallises very sluggishly (about 1 mm. in 3 days), yielding a very opaque film showing aggregate polarisation; this confused crystallisation is structurally identical with the broad needles produced so easily just below the melting point, because here and there in the mass transparent fragments may be observed having optical properties identical with those of the material produced at the higher temperature, and also because no conversion of the one material into the other occurs on standing. Since crystallisation only occurs readily at about 60°, it is necessary, in order to obtain a crystalline film rapidly, to allow the hot molten film to cool until crystallisation starts from centres, and then to warm it over the lamp until the whole has solidified.

The rotatory power of the hydrated salt, $C_{10}H_{18}N,HCl+H_2O$, was determined in aqueous and absolute alcoholic solutions. 0.4932 gram, made up to $25\cdot15$ c.c. with water at $18\cdot9^\circ$, gave $a_D-2\cdot37^\circ$ in a 200 mm. tube; 0.5451 gram, made up to $25\cdot15$ c.c. with absolute alcohol at $18\cdot9^\circ$, gave $a_D-3\cdot03^\circ$ in a 200 mm. tube; whence the following values:

	In aqueous solution.	In alcoholic solution.
C ₁₀ H ₁₃ N, HCl+H ₂ O C ₁₀ H ₁₃ N, HCl C ₁₀ H ₁₃ N, HCl	[a] _p - 66·4	[a] _D - 69·9° [a] _D - 77·4 [M] _D - 140·8

$\label{eq:local_local_local_local} \textit{Lavotetrahydroquinaldine Picrate, $C_{10}H_{18}N,C_6H_2(NO_2)_3$OH.}$

Lævotetrahydroquinaldine picrate is prepared by crystallising a mixture of the lævo-base and picric acid in the requisite proportion from hot alcohol; it forms dark yellow plates or needles melting at 148—150°, but crystals suitable for goniometrical examination could not be obtained. It is sparingly soluble in water and moderately so in alcohol, acetone, benzene, or ethylic acetate. The following analytical results were obtained with material crystallised from absolute alcohol:

0.1693 gave 0.3145 CO₂ and 0.0670 H₂O. C=50.66; H=4.39. 0.2146 ,, 0.4003 CO₂ ,, 0.0838 H₂O. C=50.87; H=4.34.
$$C_{10}H_{16}O_7N_4$$
 requires C=51.06; H=4.26 per cent.

A solution of 0.5014 gram, made with 25.2 c.c. of absolute alcohol at 20° , gave $a_D - 1.31^{\circ}$ in a 200 mm. tube, whence $[\alpha]_D - 33.0^{\circ}$ and $[M]_D - 124^{\circ}$. Since the molecular rotatory power of lævotetrahydroquinaldine in absolute alcohol is $[M]_D - 94.1^{\circ}$, it would appear that the picrate for the most part is not dissociated in alcoholic solution.

Benzoyllævotetrahydroquinaldine, $C_{10}H_{12}N \cdot CO \cdot C_6H_5$.

On suspending purified lævotetrahydroquinaldine in warm caustic soda solution and running in rather more than the calculated quantity of benzoic chloride with continual agitation, an opaque, yellowish oil separates which rapidly solidifies to a hard, crystalline mass; this is ground in a mortar and filtered, being well washed with water and dilute hydrochloric acid. The substance is best purified by crystallisation from acetone; if, as sometimes happens, a green colouring matter is produced, this is best destroyed by crystallisation from ethylic acetate. After ultimately crystallising from absolute alcohol, the benzoyl derivative is obtained in colourless crystals melting at 117.5—118°. It is very soluble in benzene and moderately soluble in cold alcohol, less so in cold acetone or ethylic acetate; it is nearly insoluble in light petroleum or boiling water. This substance is, as would be expected, appreciably more soluble than the corresponding racemic compound. The following results were obtained on analysis:

In order to obtain evidence as to the racemic nature of externally compensated benzoyltetrahydroquinaldine, it was necessary to compare the densities and crystalline forms of the active and inactive substances. The densities were determined by Retgers' method (Zeit. physikal. Chem., 1889, 3, 497), using a solution of barium mercuric iodide diluted with water; the results seem slightly more accurate than those obtained by Retgers with isomorphous mixtures, using organic liquids. The following results were obtained with crystals of benzoyllævotetrahydroquinaldine deposited from acetone or ethylic acetate solutions:

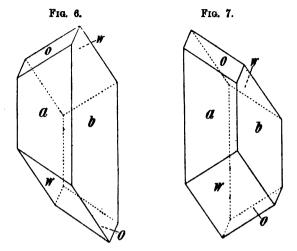
$$d_{\bullet}^{1.5} = 1.2119$$
; 1.2113; 1.2116; mean = 1.2116;

the molecular volume of the crystalline material is thus 207.16 at $14.5^{\circ}/4^{\circ}$.

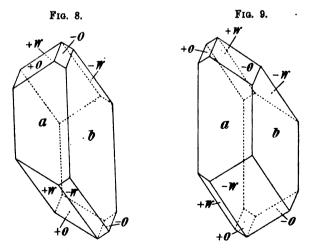
The crystallographic properties of the benzoyl derivatives of lævoand dextro-tetrahydroquinaldine were fully studied and compared; the crystals of the two substances being enantiomorphously related, as was to be expected, the following crystallographic description includes both compounds.

The optically active benzoyltetrahydroquinaldines are so soluble in benzene that good crystals could not be obtained from this solvent;

cold solutions in acetone or ethylic acetate, however, deposit on spontaneous evaporation well-developed crystals suitable for goniometrical examination. The crystals are usually elongated in the direction of



the c-axis, and then are generally developed only at one end; frequently, however, crystals of the typical habit shown in Figs. 6 and 7 are obtained, and the examination of these crystals shows them to be



hemimorphic, the b-axis being polar. The pinacoids $a\{100\}$ and $b\{010\}$ are predominant, and generally of about the same facial development; neither of these forms gives very good reflections. The form $\rho w\{\bar{1}11\}$ is usually fairly large, whilst the pyramid $\rho o\{111\}$ is quite small;

crystals exhibiting the number of faces required in the holohedral division of the monosymmetric system are often deposited from ethylic acetate solution, but the hemimorphism is generally betrayed by the unequal sizes of the faces, as in Figs. 8 and 9.

There is a very perfect cleavage parallel to $a\{100\}$, and the acute bisectrix emerges through a cleavage fragment at the edge of the field; observation of the extinction in b(010) shows that the acute bisectrix lies in the plane of symmetry at 17.5° to the face—normal to a(100). Both optic axes are visible in convergent light under a 1/12th inch oil immersion objective; the optic axial dispersion is marked, the optic axial angle for red being greater than that for blue light. The double refraction is positive in sign, and the optic axial plane is perpendicular to the plane of symmetry.

Crystalline system. - Monosymmetric: Hemimorphic.

$$a:b:c=1.0277:1:0.4261.$$

$$\beta = 88^{\circ} 15'$$
.

Forms present on benzoyllævotetrahydroquinaldine (Figs. 6 and 8). — $a\{100\}$, $b\{010\}$, $+\rho o\{111\}$ and $+\rho w\{\bar{1}11\}$; sometimes also $-\rho o\{111\}$ and $-\rho w\{\bar{1}11\}$.

Forms present on benzoyldextrotetrahydroquinaldine (Figs. 7 and 9).— $a\{100\}$, $b\{010\}$, $-\rho o\{111\}$, $-\rho w\{111\}$; sometimes also $+\rho o\{111\}$ and $+\rho w\{\bar{1}11\}$.

The following	angular	measurements	were	obtained	:
THO TOHOWING	anguiai	measurements	MOTO	ODUMENT	٠

Angle.	Number of measurements.	Limits.	Mean. observed.	Calculated.
$ao = 100:111$ $ow = 111:\overline{1}11$ $aw = \overline{1}00:\overline{1}11$ $bo = 010:111$ $oo = 111:\overline{1}11$ $bw = 010:\overline{1}11$ $ww = \overline{1}11:\overline{1}11$ $ow = 111:\overline{1}11$ $ow = 111:\overline{1}11$	36 38 29 26 21 24 19 8	67°15′— 67°59′ 41 7 — 42 15 70 3 — 71 0 68 16 — 69 11 41 56 — 43 5 67 44 — 68 39 43 8 — 44 12 117 4 —118 46 61 24 — 62 30	67°43′ 41 45 70 31 68 44 42 28 68 16 43 31 117 56 61 59	70°32′ 42 32 68 18 43 23 117 52 62 8

After melting the substance on a microscope slide under a cover slip, the liquid film can usually be cooled to the ordinary temperature without any solidification occurring; sometimes, however, crystallisation sets in whilst the film is very hot and then proceeds rapidly at the high temperature, but stops entirely when the slide cools. The crystallisation, having once started, can be caused to proceed rapidly until complete by cautiously heating the film at a temperature

below its melting point. The crystalline film consists of large, well-defined individual flakes; the larger faces of some of these are nearly perpendicular to the acute bisectrix of a fairly small optic axial angle showing positive double refraction, but those of others are nearly perpendicular to the obtuse bisectrix, in which the double refraction is apparently negative in sign. The optic axial dispersion is marked, the optic axial angle for red being greater than that for blue light. At the ordinary temperature, the liquid film solidifies very slowly indeed to a mass of interlaced needles showing aggregate polarisation; some of these needles can be seen to lie perpendicularly to the optically negative bisectrix of a large optic axial angle. Both the films obtained at high and low temperatures are probably structurally identical and also identical with the crystals deposited from solution.

The rotation constants of benzoyllævotetrahydroquinaldine are of considerable interest, and show that the introduction of the acidic group has converted the lavorotatory base into a highly dextrorotatory compound. This is the more remarkable since the piperidine bases, dextro-a-pipecoline, dextroisopipecoline, coniine, and dextroisoconline, have the specific rotatory powers [a] + 36.9°, + 33.29°, +13.79°, and +8.19° respectively, whilst their benzoyl derivatives are also dextrorotatory and have the values $[a]_D + 35 \cdot 3^\circ$, $+ 33 \cdot 35^\circ$, $+ 37 \cdot 7^\circ$, and +29.1° respectively; the introduction of the benzoyl group into the pipecolines scarcely alters the specific rotatory power (Ladenburg, Ber., 1893, 26, 854). A case somewhat similar to that of leevotetrahydroquinaldine and its benzoyl derivative has been investigated by Forster (Trans., 1898, 73, 386), who finds that dextrobornylamine having [M]_D + 69.6° yields a benzoyl derivative having the molecular rotatory power in alcoholic solution of [M]_D - 56.0°, the molecular rotatory power thus changing by 125.6°; in the case now recorded, a change of nearly 1000° in molecular rotatory power attends the conversion of the base into its benzoyl derivative. It is further of interest to note that, whilst the change of rotatory power occurs in the same sense on passing from either bornylamine or neobornylamine to its hydrochloride and then to its benzoyl derivative, the direction of the change in rotatory power alters in the case of tetrahydroquinaldine, as is shown in the following table:

	l-Tetrahydro- quinaldine[M] _▶	Bornylamine, [M] _p .	Neobornyl- amine, [M].
Base	-140.8	+69.6° +43.0 -56.0	- 47·9° - 73·8 - 114·8

The variation of the rotation constants of non-electrolytes with change of solvent has up to the present been but little studied, as, with the exception of the work of Freundler (Ann. Chim. Phys., 1895, [vii], 4, 286), few results of theoretical importance have been derived from such determinations. As, however, we show in a subsequent paper (this vol., p. 1111) that valuable information concerning the state of molecular aggregation of optically active substances is derivable from the variations in rotation constants referred to, a series of determinations of the specific rotatory powers of benzoyllævotetrahydroquinaldine in various solvents has been made. The results are stated in the following table, in which w denotes the weight of substance contained in v c.c. of solution at temperature t, and c is the concentration in grams per 100 c.c. of solution:

Solvent.	w.	v.	c.	t.	a _D .	[a] _D .	[M] _D .
Benzene ,, Chloroform Acetone Ethylic alcohol Ethylic acetate Acetic acid	0·2502 0·5007 1·0008 0·5010 0·4998 0·5002 0·5009 0·5000	25·24 25·17 25·24 25·10 25·19 25·19 25·17 25·19	0.991 1.989 3.965 1.989 1.982 1.986 1.990	28·0° 27·5 23·0 25·5 25·0 25·0 26·0 25·0	+4.96° +9.98 +19.93 +12.08 +12.55 +12.89 +13.00 +14.41	+250·2° +250·8 +251·3 +303·7 +316·6 +324·6 +326·6 +363·0	+628.0° +629.6 +630.8 +762.2 +794.6 +814.7 +819.8 +911.1

Hydrolysis of Benzoyllævotetrahydroquinaldins.—Since we proposed to prepare pure dextrotetrahydroquinaldine by hydrolysing its benzoyl derivative, and since racemisation frequently accompanies chemical change, it was desirable to ascertain whether benzoyllævotetrahydroquinaldine yields only the parent base on hydrolysis. The powdered benzoyl derivative was hydrolysed by boiling for some days with concentrated hydrochloric acid; after rendering alkaline with soda, and extracting with ether, the ethereal solution was washed with water and evaporated to dryness, hydrochloric acid being added towards the end. The crystalline hydrochloride was then ground up with acetone in an agate mortar, separated by filtration, and spread on a porous plate; it was colourless, and 0.5009 gram, dissolved in water and made up to 25.2 c.c. at 23.0°, gave $a_D = 2.63^\circ$ in a 200 mm. tube, whence $[a]_D - 66.2^\circ$. This being the specific rotatory power of the lævohydrochloride, it is obvious that no racemisation attends the hydrolysis,

II. Equilibria between Optical Isomerides and their Solutions.

Fractional Crystallisation of Crude Dextrotetrahydroquinaldins
Dextrocamphorsulphonats.

Preliminary experiments showed that, on crystallising externally compensated tetrahydroquinaldine with dextro-a-bromocamphorsulphonic acid, the first separation of crystals yielded a lævorotatory base on treatment with alkali; similarly, it was found that, on crystallising the inactive base with Reychler's dextrocamphorsulphonic acid, the first separation of crystals gave a dextrorotatory base when rendered alkaline with soda and distilled in steam. We consequently expected that, after separating the major part of the levo-isomeride as bromocamphorsulphonate, pure dextrotetrahydroquinaldine would be readily obtainable from the mother liquors by isolating the base and converting it into dextrocamphorsulphonate; by recrystallising this salt, we expected easily to obtain a pure salt of dextrotetrahydroquinaldine, and to dispense with the rather tedious process originally employed by Ladenburg (Ber., 1894, 27, 77) for preparing the dextrorotatory base. Singularly enough, however, this plan was a failure, but the results obtained are of sufficient interest to merit description.

The crude dextro-base was separated from the mother liquors and dissolved in a hot ethylic acetate solution of a molecular proportion of Reychler's dextrocamphorsulphonic acid. On cooling, a copious separation of the camphorsulphonate occurred, and this was repeatedly crystallised from hot ethylic acetate, the salt separating in colourless, acicular aggregates. The fresh crystals melt at 65-80°, but after preliminary drying in a vacuum the melting point is 125-127°; the lower melting point is due apparently to mechanically retained solvent, because the crystals do not lose appreciably in weight at 100°. The salt was recrystallised four times from ethylic acetate. the melting points, after drying, being (1) 121-123°, (2) 125-127°, (3) 125-127°, and (4) 125-127°, so that the material had been recrystallised twice after attaining the constant melting point 125-127°, and might reasonably be expected to be a pure salt. After treatment with soda and distillation in steam, the base was obtained as a colourless oil boiling at 156° under 54 mm. pressure. gave the rotatory power $a_D + 39.44^{\circ}$ in a 100 mm. tube, and since the pure lævo-base gives $a_0 - 59.24^{\circ}$ in a 100 mm, tube, still contains about one-sixth of its weight of lævo-base.

The base was therefore again converted into dextrocamphorsulphonate and crystallised from boiling acetone; the salt is very sparingly soluble in hot dry acetone, but dissolves readily if the solvent contains several per cent. of water. The first separation melted at 125—127°.

and after drying at 100° , a solution of 1 gram made up to 25 c.c. with water gave $a_{\rm D}+3\cdot60^{\circ}$ in a 200 mm. tube, whence $[a]_{\rm D}+45\cdot0^{\circ}$; the mother liquor gave a separation melting at $125-127^{\circ}$, and after drying at 100° an aqueous solution of 0.4374 gram of this, made up to 25 c.c. with water, gave $a_{\rm D}+1\cdot53$ in a 200 mm. tube, whence $a_{\rm D}+44\cdot3^{\circ}$. The main separation having $[a]_{\rm D}+45\cdot0^{\circ}$ was once more crystallised from acetone and again melted at $125-127^{\circ}$; an aqueous solution of 0.4374 gram of this in 25 c.c. gave $a_{\rm D}+1\cdot57^{\circ}$ in a 200 mm. tube, whence $[a]_{\rm D}+44\cdot9^{\circ}$. These three fractions having identical melting points and practically the same specific rotatory power, the base was again separated as before from the fraction having $[a]_{\rm D}+44\cdot9^{\circ}$. After distillation under reduced pressure, the base had the rotatory power $a_{\rm D}+53\cdot04^{\circ}$ in a 100 mm. tube, a value considerably below that obtained for the pure levo-isomeride, namely, $a_{\rm D}-59\cdot24^{\circ}$.

These results illustrate well the extreme difficulty which may be met with in isolating a pure salt of the type $dB\ dA$, from a mixture of the types $dB\ dA$ and $lB\ dA$. Had we not possessed previous knowledge of the specific rotatory power of dextrotetrahydroquinaldine, we should, on the basis of the above results, have been justified in supposing the rotatory power of the dextro-base to be $a_D + 53^\circ$ in a 100 mm. tube. It is therefore necessary to emphasise the fact that in separating a mixture of the type $dB\ dA$, $lB\ dA$, no criterion of purity is necessarily afforded by the identity of melting point or rotatory power of several consecutive fractions.

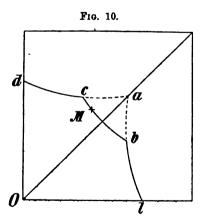
Fractional Crystallisation of Crude Dextrotetrahydroquinaldine Hydrochloride.

We have shown that lævotetrahydroquinaldine hydrochloride has the composition $C_{10}H_{13}N$, $HCl+H_2O$, whilst the racemic isomeride is anhydrous; it might therefore be expected that by crystallising the hydrochloride of the dextro-base containing a little of the lævo-isomeride, dextrotetrahydroquinaldine hydrochloride could easily be obtained in a pure state. Here again we met with failure, and again the failure was more interesting than success would have been.

A quantity of crude dextrotetrahydroquinaldine obtained in the manner described above from the mother liquors remaining after the preparation of lævotetrahydroquinaldine dextro-a-bromocamphorsulphonate was converted into hydrochloride, which was then fractionally crystallised from absolute alcohol. The first fractions consisted almost entirely of the racemic hydrochloride, which would be expected to be less soluble than its optically active components; they had $[a]_p + 6^\circ$ or $+7^\circ$, and were only mechanically contaminated with the dextrohydrochloride by reason of adherent mother liquor. These fractions

were recrystallised from absolute alcohol, and readily yielded pure racemic hydrochloride; the mother liquors in which the deutro-hydrochloride had concentrated were then added to the main mother liquor, and the fractionation continued. After a series of deposits had been obtained of this low rotatory power ($[a]_D + 6^\circ$ to 7°), the specific rotatory power suddenly rose considerably; thus a separation having $[a]_D + 6 \cdot 28^\circ$ was followed by one having $[a]_D + 41 \cdot 90^\circ$, and the succeeding fractions had specific rotatory powers varying from $[a]_D + 55^\circ$ to $+58^\circ$ in 2 per cent. aqueous solutions. Further, the repeated recrystallisation of these fractions failed on all occasions, with one exception, to yield a product having the specific rotatory power dextrotetrahydroquinaldine hydrochloride, namely, $[a]_D + 62 \cdot 8^\circ$ in aqueous solution, the specific rotatory power of the deposits varying from $[a]_D + 55^\circ$ to $+58^\circ$.

This behaviour showed that fractional crystallisation of a mixture of racemic and dextrorotatory tetrahydroquinaldine hydrochlorides from alcohol could not be used as a practical method for obtaining the pure dextro-salt; the racemic hydrochloride can be separated from the mixture until only a few per cent. of it remains with the dextro-salt, and further crystallisation fails to sensibly reduce this proportion. The explanation of this behaviour is to be found in Roozeboom's lucid discussion of the isothermals for systems consisting of a solvent, a racemic compound and its optically active components (Zeit. physikal. Chem., 1899, 28, 494). In Fig. 10 the ordinates denote



the quantity of dextro-compound, and the abscisse the quantity of levo-compound in the saturated solution; the curve *lbcd* is an isothermal representing the composition of saturated solutions of the dextro- and levo-compound and their mixtures at some particular temperature. The branches *lb* and *dc* of the curve represent solutions

in contact with levo- or dextro-material respectively, in contact, therefore, with one solid phase; the branch be represents solutions in equilibrium with the racemic compound, again, therefore, with one solid phase. The points b and c, however, represent solutions which are in equilibrium with two solid phases, namely, the racemic and one optically active component. Suppose, we start with a solution containing both dextro- and levo-material in the proportion corresponding to the point M on the curve; on crystallisation, the solution will deposit racemic compound, and the composition of the saturated mother liquor will change in the direction of the point c; after the composition at c is reached, the subsequent fractions will be of identical composition and specific rotation, both dextro- and racemic salt being deposited in a fixed proportion, and the solution retaining the composition at c until the whole of the solvent has evaporated. These considerations hold if the temperature of crystallisation remains constant, and in our attempts to isolate the dextro-salt from the mixture, crystallisation always occurred at the ordinary temperature; in spite of slight temperature fluctuations, we were in general unable to change the composition of the mixture to any serviceable extent from that at the point c. This is apparently the first recorded instance in which equilibrium in contact with an optically active and racemic phase at the point c has interposed practical difficulty, and we hoped to overcome the difficulty by sowing dextrohydrochloride into supersaturated solutions obtained by lowering the temperature or by cooling saturated solutions in contact with the dextrosalt so that the solution becomes a labile one of composition lying upon the branch ac. Only on one occasion, however, did we succeed in getting a separation of pure dextrotetrahydroquinaldine hydrochloride. This is somewhat noteworthy, because Kipping and Pope observed just the converse behaviour with mixtures of potassium sodium dextro- and lævo-tartrates (Trans., 1899, 77, 45), and pointed out the ease with which "a racemic compound might, under certain conditions, be resolved into its optically active components by simple crystallisation at temperatures at which the racemic compound is more stable than the mixture of the two optically active salts."

Attempts were made to change the composition of the solutions of the mixed hydrochlorides from that represented by the point c by alternate crystallisations from two solvents, on the supposition that the composition at this point would differ for various solvents; our efforts in this direction were not successful, the only useful solvent besides alcohol being a mixture of alcohol and acetone.

Fractional Crystallisation of Mixtures of Dextro- and Racemic Benzoyltetrahydroquinaldine.

In spite of our failure to isolate pure dextrotetrahydroquinaldine hydrochloride in quantity from its mixture with the racemic compound and the consequent expectation of a similar behaviour with the benzoyl derivatives, we were able easily to obtain benzoyldextrotetrahydroquinaldine in quantity by fractionally crystallising a mixture of this substance with its racemic isomeride. Since we have previously shown that no racemisation occurs on hydrolysing benzoyllævotetrahydroquinaldine, we could readily obtain pure dextrotetrahydroquinaldine in quantity from its benzoyl derivative.

The conversion of the mixture of dextro-base with a much smaller proportion of its lævo-isomeride into benzoyl derivative is effected as previously described (p. 1073); the benzoyl derivative is then systematically fractionated from its hot acetone solution by recrystallising the early separations, which consist largely of the racemic compound, and adding the optically active mother liquors to the main solution. After the greater part of the racemic material present has been eliminated, the subsequent deposits consist of nearly pure benzoyldextrotetrahydroquinaldine, whilst occasionally a separation of low specific rotatory power occurs; by continuing the fractionation and determining the specific rotatory power of each deposit, practically all of the original benzoyl derivative may be obtained in two lots, the one inactive, and the other baving $[a]_D - 247.4^\circ$ in a 2 per cent. benzene solution at 16°. Since our specimen of pure benzoyllævotetrahydroquinaldine had $[a]_D + 247.3^\circ$ at 15° in benzene solution, the material of $[a]_p - 247.4^\circ$ is obviously a pure substance. In this case, therefore, the existence of the equilibrium point c (Fig. 10) causes no practical difficulty, owing, doubtless, to a greater facility of supersaturation.

III. DEXTROTETRAHYDROQUINALDINE.

Benzoyldextrotetrahydroquinaldins.

The general properties of benzoyldextrotetrahydroquinaldine need no separate description; its crystalline form has already been discussed (p. 1074), and analytical results proving its composition have been obtained.

The determinations of the density of benzoyldextrotetrahydroquinaldine were made in the same way as were those of the antipodes and with the following results:

 $d_{A}^{14.5} = 1.2111$; 1.2115; 1.2115. Mean = 1.2114.

The molecular volume at 14.5°/4° is thus 207.20; the mean density and

molecular volume differ by only 0.02 per cent. from the corresponding values obtained for benzoyllævotetrahydroquinaldine.

Benzoyldextrotetrahydroquinaldine is highly lævorotatory, and its rotation constants are given in the following table:

Solvent.	w.	v.	c.	t.	α _D .	[a] _D .	[M] _D .
Benzene	0.2502	25.24	0.991	18°	- 4·88°	- 246·1°	- 617·7°
,,	0.5007	25.24	1.984	18	- 9.80	- 247.0	- 620.0
,,	1.0005	25.24	3.964	18	- 19.70	- 248.5	- 623.7
,,	0.5000	25.24	1.981	17	-9.76	- 246.3	- 618 2
,,	1.0000	25.24	3.962	17	-19.77	- 249.5	- 626.2
Chloroform	0.2000	25.25	1.980	17	-12.23	- 308.8	- 775 1
Acetone	0.5000	25.25	1.980	17	-12.64	- 319.2	-801.1
Ethylic alcohol	0.2000	25.25	1.980	17	- 12.97	- 327 . 5	- 822.0
Ethylic acetate	0.4995	25.24	1.979	17	- 13 12	-331.5	- 832 0
Acetic acid	0.5000	25.25	1.980	17	-14.60	- 368.6	- 925.2

A comparison of these numbers with those obtained with the antipodes shows that the two sets differ arithmetically but slightly, the difference being attributable to the different working temperature. In both cases, the solutions in glacial acetic acid show far the highest rotation constants.

Dextrotetrahydroquinaldine.

For the preparation of this base, finely-powdered benzoyldextrotetra-hydroquinaldine is heated in a reflux apparatus with excess of concentrated hydrochloric acid; after several days' heating, a copious separation of benzoic acid occurs on cooling, and the hydrolysis is complete. Slight excess of soda is added and the product distilled in a current of steam; the base is extracted with ether and purified as before described; the purity of the product was ascertained by a determination of its density and specific rotatory power. The density was found to be d_{\star}^{ac} 1.01926, and the rotatory power was $a_{\rm D} + 59.21^{\circ}$ in a 100 mm. tube at 20°, whence $[a]_{\rm D} + 58.09$ at 20°. Ladenburg gives the rotatory power, $a_{\rm D} + 58.35^{\circ}$ in a 100 mm. tube at 16°, for this base, and calculates the specific rotatory power as $[a]_{\rm D} + 55.99^{\circ}$; the density number, d_{\star}^{1c} 1.042, which he uses is somewhat too high (Ber., 1894, 27, 76).

Dextrotetrahydroquinaldine Hydrochloride, $C_{10}H_{13}N$, $HCl + H_2O$.

The hydrochloride of dextrotetrahydroquinaldine was prepared in the same way as that of the lævo-isomeride. It crystallises in large, orthorhombic monohydrated tablets which melt at 196.5—197.5°, and are crystallographically indistinguishable from the crystals of the lævo-isomeride (Figs. 1 and 2, p. 1070).

The specific rotatory power of the salt dried at 100° was determined in aqueous solution; 0.4806 gram of the anhydrous salt, made up to 25.3 c.c. with water at 21.4°, gave $a_D + 2.51^\circ$ in a 200 mm. tube. The specific rotatory power is thus $[a]_D + 66.1^\circ$, which compares perfectly well with the value $[a]_D - 66.4^\circ$ obtained for lævotetrahydroquinaldine hydrochloride (p. 1072).

IV. MOLECULAR ROTATORY POWERS OF SALTS OF OPTICALLY ACTIVE BASES WITH OPTICALLY ACTIVE ACIDS.

A simple law should connect the molecular rotatory powers of optically active salts of the type dB dA and lB dA, in fairly dilute aqueous solutions, provided that the base and acid, B and A, are so strong that the salts are practically wholly dissociated. algebraic difference between the molecular rotatory powers of the two salts should be equal to twice the molecular rotatory powers of the hydrochloride or similar salt of the active base, whilst the algebraic sum should be equal to twice the molecular rotatory power of a metallic salt of the active acid. Since the truth of this consequence of the electrolytic dissociation hypothesis has previously only been tested by Walden upon salts of feeble bases, like morphine (Zeit. physikal. Chem., 1894, 15, 206), it seemed desirable to prepare salts of the strong bases, dextroand levo-tetrahydroquinaldine, with a powerful optically active acid, when the principle enunciated above should be found to hold even more rigidly than in the case referred to. For this purpose, the salts of dextro- and leevo-tetrahydroquinaldine with Reychler's dextrocamphorsulphonic acid were prepared; the former salt was also required in order to compare its properties with those of the impure compound obtained in the fractional crystallisation of the mixture.

Dextrotetrahydroquinaldine Dextrocamphorsulphonate, $C_{10}H_{13}N, C_{10}H_{15}O \cdot SO_{3}H$.

Dextrotetrahydroquinaldine dextrocamphorsulphonate is obtained by crystallising a benzene solution of the component base and acid in long, colourless, flat prisms melting at 128—129°; the prism zone is composed of six faces, whilst rather obliquely placed end faces complete the crystal. An optic axis is observed to emerge through the large face, and the extinction in this face is practically parallel with the longer sides; the crystals are very possibly anorthic, but good crystals could not be obtained for measurement. The salt is soluble in the ordinary organic solvents, including carbon bisulphide and ethylene dibromide. The following analytical results were obtained with material dried at 100°:

 $C_{20}H_{29}O_4NS$ requires C = 63.32; H = 7.65; S = 8.64 per cent.

The specific rotation was determined in aqueous solution: 0.5077 gram, made up to 25 c.c. with water at 19.1° , gave $a_D + 1.85^{\circ}$ in a 200 mm. tube; whence $[a]_D + 45.7^{\circ}$ and $[M]_D + 173.3^{\circ}$.

In discussing the fractional crystallisation of a mixture of the dextro-camphorsulphonates of dextro- and lævo-tetrahydroquinaldine, it was pointed out (p. 1079) that we were unable to obtain the dextrocamphorsulphonate of a higher specific rotatory power than $[a]_{\rm p} + 45 \cdot 0^{\circ}$ in aqueous solution, and that this salt yielded a base having the rotatory power $a_{\rm p} + 53^{\circ}$ in place of $+59^{\circ}$; since it is now shown that dextrotetrahydroquinaldine dextrocamphorsulphonate has $[a]_{\rm p} + 45 \cdot 7^{\circ}$, it is evident that the material previously obtained was, as we stated, still contaminated with salt of the lævo-base.

Lavotetrahydroquinaldine Dextrocamphorsulphonate, $C_{10}H_{13}N$, $C_{10}H_{15}O\cdot SO_8H$.

Lævotetrahydroquinaldine dextrocamphorsulphonate is prepared by crystallising the requisite quantities of the base and acid together from benzene solution; it separates in colourless, flattened needles melting at 137—138°. The needles are square ended with truncated corners; the extinction in the large face is straight with the sides, and a bisectrix emerges perpendicularly through the face. The following analytical results were obtained with material dried at 100°:

```
0.2022 gave 0.4680 CO<sub>2</sub> and 0.1416 H<sub>2</sub>O. C = 63·12; H = 7·78. 0.1209 , 0.2802 CO<sub>2</sub> , 0.0882 H<sub>2</sub>O. C = 63·21; H = 7·83. 0.4415 , 0.2838 BaSO<sub>4</sub>. S = 8·85. C<sub>20</sub>H<sub>20</sub>O<sub>4</sub>NS requires C = 63·32; H = 7·65; S = 8·64 per cent.
```

0.5073 gram, made up to 25 c.c. with water at 19.1°, gave $a_D = 0.74^{\circ}$ in a 200 mm. tube, whence $[a]_D = 18.3^{\circ}$ and $[M]_D = 69.5^{\circ}$.

Ammonium Dextrocamphorsulphonate, C₁₀H₁₅O·SO₃NH₄.

The ammonium salt of dextrocamphorsulphonic acid has been described by Reychler (*Bull. Soc. Chim.*, 1898, [iii], 19, 120); we obtained it in long, colourless needles which, after drying at 100°, gave analytical results agreeing with those required for the above formula. The following rotation determinations were made:

0.2503 gram, made up to 25 c.c. with water at 16°, gave $a_D + 0.12^{\circ}$ in a 200 mm. tube; whence $[a]_D + 21.0^{\circ}$.

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0.5000 gram, made up to 25 c.c. with water at 18°, gave $a_D + 0.83^{\circ}$ in a 200 mm. tube; whence $[a]_D + 20.7^{\circ}$.

1.0008 grams, made up to 25 c.c. with water at 18°, gave $a_D + 1.65^{\circ}$ in a 200 mm. tube; whence $[a]_D + 20.6^{\circ}$.

Since we are dealing all through with solutions of about 2 per cent., we may take for comparison with other salts the values $[\alpha]_D + 20.7^\circ$ and $[M]_D + 51.7^\circ$. The following table gives the specific and molecular rotatory powers of the various salts of dextrocamphorsulphonic acid with which we are concerned:

Salt.	[α] _D ,	[M] ₀ .
d-C ₁₀ H ₁₂ N,d-C ₁₀ H ₁₅ O·SO ₂ H l-C ₁₀ H ₁₈ N,d-C ₁₀ H ₁₅ O·SO ₃ H l-C ₁₀ H ₁₈ N,HCl NH ₃ d-C ₁₀ H ₁₈ O·SO ₂ H	+ 45·7° - 18·8	+ 178 ·8° - 69 ·5
<i>l</i> -C ₁₀ H ₁₈ N,HCl NH ₂₆ <i>d</i> -C ₁₀ H ₁₅ O·SO ₃ H	- 6 6 · 4 + 20 · 7	- 121 7 + 51 7

The algebraic difference between the molecular rotatory powers of salts (1) and (2) is 242.8° and the half of this, namely, 121.4°, should be equal to the molecular rotatory powers of active tetrahydroquinaldine hydrochloride, namely, 121.7°. Further, the algebraic sum of molecular rotatory powers (1) and (2) is 103.8, and the half of this, namely, 51.9°, should be equal to the molecular rotatory power of ammonium dextrocamphorsulphonate, namely, 51.7°. The agreement even in these comparatively concentrated solutions is very close.

V. Externally Compensated Tetrahydroquinaldine.

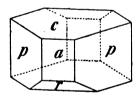
For the preparation of the tetrahydroquinaldine used in the present work, quinaldine was reduced with tin and hydrochloric acid essentially as described by Walter (Ber., 1892, 25, 1261); when the reduction was complete, slight excess of soda was added and the liquid subjected to prolonged distillation in a current of steam. The tetrahydroquinaldine was extracted from the distillate with ether, the ethereal solution dried over potash and fractionally distilled; the fraction boiling at 240—250° was taken as containing all the hydroquinaldine and is sufficiently pure for immediate resolution into its optically active components as described above.

Racemic Tetrahydroquinaldine Hydrochloride, C10H15N,HCl.

A quantity of the crude base boiling at 240—250° was dissolved in large excess of hydrochloric acid and the solution allowed to crystal-

lise: the deposited hydrochloride was crystallised a number of times from absolute alcohol and then melted at 196-197.5°. This salt was prepared by Fischer and Steche (Annalen, 1887, 242, 358) and described as not very soluble in water, but easily soluble in alcohol; it is, however, less soluble in alcohol than in water. Our analytical results show that the salt has the composition C10H18N,HCl, as deposited from aqueous or alcoholic solutions; it is consequently a true racemic compound, because its optically active components under similar conditions crystallise with water. It separates on spontaneous evaporation of its pure aqueous or alcoholic solution either in small, colourless, transparent crystals of rhombohedral habit, or in long, thin needles, both melting at 196-197.5°. These crystals are very poorly developed and the faces show considerable striation; on microscopic examination, they are usually found to be composite, a lamellated twin structure somewhat resembling that characteristic of labradorite being observed. The goniometrical examination of these crystals gave no result other than that the crystals are geometrically pseudorhombohedral in accordance with the lamellation detected microscopically. Large crystals better suited for measurement are obtained by spontaneous evaporation of a solution of the salt in hydrochloric acid; these consist of large, colourless, transparent tablets of poor facial The form $c\{001\}$ is dominant (Fig. 11) and the development.

Fig. 11.



prism $p\{110\}$ is also well developed; the pinacoid $a\{100\}$ is usually smaller, and the faces of the dome $r\{\overline{1}01\}$ are only observed as narrow replacements. There is an extremely perfect cleavage parallel to $c\{001\}$ and, when hacked in other directions, the crystals merely shear parallel to the cleavage. A bisectrix of positive double refraction emerges nearly normally to c(001), but the orientation of the optic axial plane could not be ascertained.

Crystalline system.—Monosymmetric.

$$a:b:c=0.934:1:0.935.$$

$$\beta = 71^{\circ} 46'$$
.

Forms observed.— $a\{100\}$, $c\{001\}$, $p\{110\}$, and $r\{101\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
ap = 100:110	31	40°48′— 42° 7′	41°35′	
$pp = 110 : \bar{1}10$	18	96 4 - 97 52	96 58	96°50′
$pp = 110:1\bar{1}0$	15	82 26 — 84 1	83 19	88 10
ac = 100:001	42	70 47 — 72 12	71 32	71 46
$cr = 001 : \overline{1}01$	81	53 42 — 55 26	54 42	54 9
$ar = 100:10\overline{1}$	38	53 6 — 55 13	54 5	–
cp = 001:110	44	75 19 — 77 14	76 28	_
$\hat{cp} = 00\bar{1}:110$	14	102 54 104 7	103 29	103 32
$pr = 110:10\bar{1}$	8	63 0 64 56	63 49	63 58

After melting the racemic hydrochloride, it solidifies whilst hot less readily than the leevo-isomeride, but when cold solidifies with distinctly greater rapidity; it is quite easy to obtain a liquid film of the racemic substance at the ordinary temperature, but after 48 hours most of the liquid has crystallised. On allowing the liquid film to cool considerably below the melting point and then again warming, the whole may soon be made to crystallise; crystallisation proceeds from centres and results in the production of broad, individual flakes, which are usually striated in a direction parallel to the extinction. The strike are parallel to the trace of the optic plane in the fragment, and a bisectrix emerges nearly normally to the face; the optic axial axes are outside the field, and the double refraction of the bisectrix, probably the obtuse one, is of positive sign. As cooling proceeds, the plates crack considerably along lines perpendicular to the direction of growth. Optically, this material is very similar to the orthorhombic plates of the lævo-hydrochloride, but morphologically it seems very different, the square plates never being observed; the inactive material produced at the high temperature does not fall to pieces during cooling in the violent manner affected by the optically active substance.

On rapidly cooling the molten film to the ordinary temperature, it remains liquid, but after a day or so a fringe of the modification described above, which polarises brilliantly, forms round the edge of the preparation and subsequently a macroscopically opaque growth makes its appearance in the body of the film; this growth consists of minute, square-ended needles showing oblique extinction and, being of low double refraction, polarises far less brilliantly than the first-described modification; the needles exhibit an oblique optic axial emergence and are interlaced in a highly confused manner. After several days, this modification occupies nearly the whole of the film and encroaches upon the brilliantly polarising fringe, the latter

apparently becoming converted into the former. The externally compensated hydrochloride is therefore almost certainly dimorphous.

Racemic Tetrahydroquinaldine Picrate, C10H18N,C6H2(NO2)3.OH.

Racemic tetrahydroquinaldine picrate is obtained by crystallising the externally compensated base with the requisite quantity of picric acid from absolute alcohol; it is more sparingly soluble in organic solvents and in water than the picrate of the lævo-base. The crystals deposited from the alcoholic solution melt at $153-154^{\circ}$ and do not give good results on measurement; they are apparently anorthic and consist of a predominant form $a\{100\}$, a smaller one, $c\{001\}$, and still smaller ones, $p\{110\}$ and $p'\{\bar{1}10\}$. The approximate angles are:

```
      ac = 100:001 = 74^{\circ} 54'
      ap = 100:110 = 32^{\circ} 13'

      cp = 001:110 = 81 20
      pp' = 110:110 = 79 0

      cp' = 001:110 = 78 6
      ap' = 100:110 = 68 47
```

There is a perfect cleavage parallel to c(001) and the acute bisectrix emerges through c(001); the optic axial angle is large, the double refraction is negative in sign, and the optic axial dispersion is so marked that no definite extinction is observed for white light in c(001). The extinction in a(100) is nearly straight with the edge ac, and the optic axial plane is nearly parallel to a(100). The following analytical results were obtained with material crystallised from alcohol:

```
0.2055 gave 0.3823 CO<sub>2</sub> and 0.0829 H<sub>2</sub>O. C=50.74; H=4.48. 0.2107 ,, 0.3933 CO<sub>2</sub> ,, 0.0825 H<sub>2</sub>O. C=50.91; H=4.35. C_{16}H_{16}O_7N_4 requires C=51.06; H=4.26 per cent.
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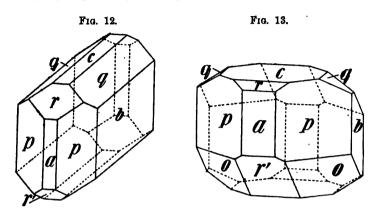
Externally Compensated Tetrahydroquinaldine, C10H18N.

Carefully purified racemic tetrahydroquinaldine hydrochloride is distilled in a current of steam with addition of a slight excess of soda; the distillate is extracted with purified ether, the ethereal solution dried with potash, and the ether distilled off. The residual nearly colourless oil is then distilled under reduced pressure and practically all distils at 196° under 207.5 mm. pressure. The base has the same density as its levo-component, and its physical properties are dealt with fully in a subsequent paper, in which it is shown that this base is merely a mixture of the two optically active constituents.

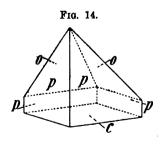
Racemic Benzoyltetrahydroquinaldine, C₁₀H₁₂N·CO·C₆H₅.

This substance has been prepared from tetrahydroquinaldine by Walter (Ber., 1892, 25, 1293), using the Schotten-Baumann reaction. It separates on spontaneous evaporation of its cold ethylic acetate

solutions in magnificent, lustrous, monosymmetric prisms (Fig. 12) melting at $117-118^{\circ}$, and showing the form $b\{010\}$ dominant; the forms $p\{110\}$ and $q\{011\}$ are the next largest forms present, whilst the pinacoid $a\{100\}$ is always small and frequently absent. The pinacoid $c\{001\}$ is well developed and gives good results on measurement; the form $r\{101\}$ is generally well represented, whilst the form $r'\{\bar{1}01\}$ is



poorly developed and rarely observed. The crystals deposited from solutions in benzene (Fig. 13) differ greatly in habit from those obtained from ethylic acetate, and lend themselves better to crystallographic measurement than do the latter; they exhibit the form $p\{110\}$ predominant, and also show $r'\{\bar{1}01\}$ and $o\{\bar{1}11\}$ well developed, whilst the pinacoids $a\{100\}$ and $b\{010\}$ are comparatively small and frequently



absent. The facial development of the form $r\{101\}$ is less than that of $r'\{101\}$. Crystals are frequently deposited from benzene solution of the hemihedral habit depicted in Fig. 14; these consist of parts of the forms $c\{001\}$, $o\{111\}$, and $p\{110\}$. No indications of pyroelectrical properties could be obtained to show that this habit is due to hemihedrism, so that it is probably due merely to abnormal conditions of growth.

Crystalline system.—Monosymmetric.

a:b:c=0.6768:1:0.6675.

 $\beta = 81^{\circ} 4'$.

Forms observed.— $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r\{101\}$, $r'\{\overline{1}01\}$ and $o\{\overline{1}11\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$ap = 100:110$ $bp = 010:110$ $pp = 110:1\overline{10}$ $qp = 110:1\overline{10}$ $qq = 001:011$ $qq = 011:0\overline{11}$ $qq = 011:0\overline{11}$ $qq = 011:0\overline{11}$ $qq = 110:011$ $pq = 110:10\overline{1}$ $pq = 110:10\overline{1}$ $pq = 100:10\overline{1}$ $qq = 001:\overline{10}$ $qq = 001:\overline{11}$ $qq = 001:\overline{11}$	7 42 35 48 17 34 25 52 51 12 16 7 9 52 4 6 11	33°16′—34° 9′ 56° 0 —56° 39° 67° 7 —67° 54° 33° 15′—33° 34° 56° 1 —56° 59° 66° 17′—67° 20° 49° 57′—50° 45′ 78° 16′—79° 0° 50° 38′—51° 32° 57° 0 —58° 2° 65° 3 —65° 58° 56° 22′—57° 6° 40° 12′—41° 1° 39° 29′—40° 56° 48° 41′—49° 12° 49° 86′—50° 14° 82° 19′—82° 54° 41° 58′—42° 55°	33°42′ 56 17 67 29 83 24 56 27 66 51 50 19 78 38 51 3 57 33 65 37 56 49 40 41 40 12 48 56 49 57 82 36 42 24	38°46′ 56 14 67 31 56 36 66 48 50 23 78 34 57 38 65 34 56 48 40 52 49 0 49 55 82 38 42 26 55 1
ab = 100: 111 co = 001: 111 op = 111: 110 cp = 001: 110 r'o = 101: 111 oo = 111: 111 bo = 010: 111	8 19 19 26 4 12	54 47 —55 10 53 42 —54 32 42 54 —43 39 82 4 —83 6 26 55 —27 30 53 29 —54 26 62 18 —63 25	54 59 54 10 48 14 82 33 27 14 53 58 62 55	54 15 43 10 82 35 27 3 54 7 62 57

The extinctions in the faces b(010) and p(110) are practically straight with the side ap. The obtuse bisectrix emerges nearly normally through $a\{100\}$ and the obtuse bisectrix is observed through a section hacked nearly perpendicular to the zone [001]; the optic axial angle is large and the double refraction is negative in sign. The optic axial dispersion is slight and the angle for blue light is greater than that for red; the plane of symmetry is the optic axial plane.

After melting, the substance solidifies fairly readily at high temperatures, and the whole film may be caused to crystallise by alternate heating and cooling; if, however, the film be rapidly cooled, it may be obtained at the ordinary temperature as a liquid film which crystallises extremely sluggishly. The crystalline film obtained at high temperatures is composed of long needles radiating from centres;

these extinguish nearly straight with the direction of growth and, on cooling, crack extensively in different directions. Most of the crystalline individuals lie nearly perpendicular to the positive obtuse bisectrix of the optic axial angle and the optic axial plane is parallel to the direction of growth. Sometimes the acute bisectrix emerges nearly normally to the surface of the crystal fragment; the optic axial angle is large and the optic axial dispersion slight. The double refraction is negative in sign. The optical properties of this modification agree closely with those of the crystals deposited from solution, and the two are structurally identical, so that externally compensated benzoyltetrahydroquinaldine melts and solidifies as a racemic compound. The molten film at ordinary temperatures crystallises very slowly, yielding a mass of needles which shows aggregate polarisation.

The density of the crystals was determined as in the case of those of the optically active constituents with the following results:

 $d^{14}_{S} = 1.2373$; 1.2380; 1.2373. Mean = 1.2375.

The molecular volume at $14\cdot5^\circ/4^\circ$ is thus 202·8. Since the optically active benzoyltetrahydroquinaldines have the molecular volume 207·2 at the same temperature in the crystalline state, it is obvious that the crystals of the racemic substance conform to Liebisch's rule (*Annalen*, 1895, 286, 140), their density being greater than that of their optically active components. In the formation of crystalline racemic benzoyltetrahydroquinaldine from its crystalline optically active components at $14\cdot5^\circ$, a contraction of about $2\cdot14$ per cent. in volume occurs.

VI. MELTING POINTS OF OPTICALLY ACTIVE AND EXTERNALLY COMPENSATED ISOMEBIDES.

The great interest which has been imported into the question of the melting points of optically active and externally compensated isomerides by the recent work of Roozeboom (Zeit. physikal. Chem., 1899, 28, 505) rendered desirable the investigation of the melting points of the hydrochlorides and benzoyl derivatives of the tetrahydroquinaldines.

Careful determinations of the melting points of highly purified racemic and optically active tetrahydroquinaldine hydrochlorides gave the values 196—197.5° and 196.5—197.5° respectively; the melting point of the racemic material is not quite so sharp as that of the dextro- or lævo-component. An intimate mixture of about equal weights of racemic and lævo-material melted at 180—184°.

Similarly, active benzoyltetrahydroquinaldine melted at 117.5—118.5° and the racemic material at 117—118°, the racemic again melting less sharply than the active isomerides. A mixture of about equal parts of each melted at 108—110°.

Although the active and inactive isomerides melt at practically the same temperature, the externally compensated substance melts as a racemic compound, and the melting point curves for the mixtures would seem to belong to Roozeboom's Type 2; attention does not seem to have been drawn previously to examples of this type.

Our thanks are due to the Research Fund Committee of the Chemical Society for grants enabling the purchase of materials used in the foregoing work.

Goldsmiths' Institute
New Cross.

CIX.—The Application of Powerful Optically Active Acids to the Resolution of Externally Compensated Basic Substances. Resolution of Tetrahydroparatoluquinaldine.

By WILLIAM JACKSON POPE AND EDMUND MILTON RICH.

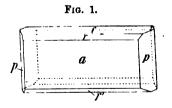
THE ease with which levotetrahydroquinaldine can be separated from the externally compensated base by the use of dextro-a-bromocamphorsulphonic acid (Pope and Peachey, this vol., p. 1066), suggested that interesting results might be obtained by applying the same method to Doebner and von Miller's externally compensated tetrahydroparatoluquinaldine (Ber., 1883, 16, 2464); this base, which is described as being an oil at ordinary temperatures, we find to be crystalline and to melt at 31-32°. When a half molecular proportion of ammonium dextro-a-bromocamphorsulphonate is added to a solution of one molecular proportion of racemic tetrahydroparatoluquinaldine hydrochloride, the levo-base separates as the bromocamphorsulphonate, just as in the case of tetrahydroquinaldine, and this lævo-base melts at 52-53°. This method, which is new in principle, should prove of service in similar cases and has already been applied to the preparation of dextrotetrahydro-β-naphthylamine (Proc., 1899, 15, 170). The crude dextro-base remaining in the mother liquors can be subsequently isolated as hydrochloride, and from this salt the dextro-base may be separated in the pure state.

I. LEVOTETRAHYDROPARATOLUQUINALDINE.

$\label{eq:loss_loss} Law otetra hydroparatoluquinal dine Dextrobromo camphor sulphonate, \\ C_{11}H_{15}N, C_{10}H_{14}BrO\cdot SO_3H.$

On adding an aqueous solution of one molecular proportion of ammonium dextro-a-bromocamphorsulphonate to a warm, aqueous solution of two molecular proportions of racemic tetrahydroparatoluquinaldine hydrochloride, an oil separates which solidifies to a crystalline mass as the solution cools. This crude lævotetrahydroparatoluquinaldine dextro-a-bromocamphorsulphonate is obtained as a mass of colourless needles after several recrystallisations from hot dilute alcohol. It melts at 195—196°, is moderately soluble in water or alcohol, and when dry is sparingly soluble in acetone or ethylic acetate; if a little moisture is present, however, the solubility increases very considerably. The following analytical results were obtained with the salt dried at 100°:

On allowing its cold solution in a mixture of ethylic acetate and alcohol to evaporate spontaneously, the salt separates in large, colourless, transparent prisms (Fig. 1) belonging to the monosymmetric system;



the form $a\{100\}$ is predominant and the prism $p\{110\}$, although small, is usually the next largest form present. The pinacoid $c\{001\}$ is well-developed, whilst the forms $r\{101\}$ and $r'\{\bar{1}01\}$ are present only as narrow replacements; the faces of the crystals are always more or less conchoidal in character and give very poor results on measurement. There is a perfect cleavage parallel to c(001) and the faces of the form $a\{100\}$ are striated parallel to the trace of the cleavage plane.

Crystalline system. -- Monosymmetric.

$$a:b:c=2.1766:1:1.2556.$$

$$B = 78^{\circ} 58'$$
.

Forms observed.— $a\{100\}$, $c\{001\}$, $p\{110\}$, $r\{101\}$, and $r'\{\overline{1}01\}$.

The following angular measurements were obtained:

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$ar = 100:101$ $cr = 001:101$ $ar' = 100:10\overline{1}$ $cr' = 001:\overline{1}01$ $ap = 100:110$ $pp = 110:\overline{1}10$ $pr = 110:101$ $pc = 110:001$ $pr' = 110:10\overline{1}$	36 38 19 14 42 20 9 15	51° 4'—52°59' 26 11 —27 43 67 58 —69 2 31 44 —33 7 64 6 —65 58 49 21 —50 45 74 23 —75 31 84 58 —86 2 80 26 —81 34	51°57′ 27 1 68 34 32 23 64 55 50 7 74 58 85 26 80 57	68°34′ 32 28 — 50 10 74 51 85 21 81 5

The optic axial plane is the plane of symmetry and one optic axis emerges nearly normally through a cleavage plate parallel to c(001); the other optic axis is seen to emerge through a(100), but not perpendicularly to the face. The optic axial dispersion is slight; the bisectrix emerging through a(100) is of positive sign and since this is the obtuse bisectrix the double refraction is negative in sign.

After melting the substance on a microscope slide under a cover slip, it crystallises with great reluctance from the edge of the preparation in long, flat, striated needles; crystallisation is hastened considerably by alternate heating and cooling. The optic axial plane lies across the longer dimension of the needles and the acute bisectrix sometimes emerges nearly normally to the plate; the double refraction is negative in sign. Usually one optic axis only can be seen emerging through the needle and then the obtuse bisectrix of positive double refraction emerges in the microscope field. The crystalline film is thus crystallographically identical with the material deposited from solution.

Lævotetrahydroparatoluquinaldine, CMe·CH:C·CH₂·CH₂ CH—CH:C·NH·CHMe·

Carefully purified levotetrahydroparatoluquinaldine dextro-a-bromocamphorsulphonate is dissolved in warm water and a slight excess of soda added, when the base separates as a colourless oil which solidifies completely on cooling; the white, crystalline mass is collected on the pump, repeatedly washed with cold water, and dried in a vacuum desiccator. On dissolving it in petroleum boiling at 25—40°, and allowing the solution to evaporate spontaneously in the air, levotetrahydroparatoluquinaldine separates in magnificent, lustrous, monosymmetric prisms (Fig. 2) several centimetres in length; it melts at 52—53°.





The crystals are enantiomorphously related to those of dextrotetrahydroparatoluquinaldine, described later, and represented in Fig. 3; the forms $a\{100\}$, $r\{101\}$, and $r'\{101\}$ are dominant, sometimes the one and sometimes the other being the larger. Usually, the crystals are only completed at the one end, that, namely, on which the form $o-\{111\}$ is developed; the other end is frequently ragged or obliterated by an hour-glass shaped structure which grows from it into the crystal. Sometimes, however, the form $b+\{010\}$ is present. Although the substance volatilises fairly rapidly in the air, yet the faces give fairly satisfactory goniometrical results.

Crystalline system.—Monosymmetric: Hemimorphic.

$$a:b:c=3.2742:1:1.4339.$$

$$\beta = 86^{\circ} 2'$$
.

Forms observed on lewotetrahydroparatoluquinaldine.— $a\{100\}$, $r\{101\}$, $r'\{101\}$, $b+\{010\}$, and $a'-\{111\}$.

Forms observed on dextrotetrahydroparatoluquinaldine.— $a\{100\}$, $r\{101\}$, $r'\{10\overline{1}\}$, $b-\{010\}$, and $o+\{11\overline{1}\}$.

The following angular measurements were made on crystals of both the lævo- and dextro-isomerides:

Angle.	Number of observations.	Limits.	Меап.	Calculated.
ar = 100:101 $ar' = 100:10\overline{1}$ $rr' = 101:\overline{1}01$ $ao = 100:11\overline{1}$ $or = \overline{1}01:101$ $or' = \overline{1}11:\overline{1}01$ $oo = \overline{1}11:11\overline{1}$ br = 010:101 ab = 100:010	37 28 35 16 32 14 16 12	62°44′—63°38′ 69 21 —70 2 46 49 —47 86 77 86 —78 42 65 36 —66 42 52 58 —53 36 72 58 —73 49 89 45 —90 21 89 40 —90 17	63° 3′ 69 43 47 14 78 9 66 6 53 16 73 21 90 3 90 1	69°43′

The optic axial plane is the plane of symmetry and one optic axis is seen emerging through the face a(100); the optic axial angle is large, and the optic axial dispersion slight. The double refraction is negative in sign and fairly strong. After melting on a microscope slide under a cover slip, the base solidifies readily from centres in long needles, which extinguish parallel to the direction of growth; the optic axial plane is perpendicular to the direction of growth, and the optically positive bisectrix of a large optic axial angle emerges in the field. These long needles alternate with material showing aggregate polarisation. This crystalline modification is identical with that deposited from petroleum solution.

The following analytical results were obtained:

The specific rotatory power was determined in various solvents, and the results are stated in the following table:

Solvent.	t.	10.	v.	α _D , 200 mm.	[α] _D .	[M] _D .	[M] _D , l-C ₁₀ H ₁₈ N.
Benzene	21°	0·5002	25·3	-3·20°	-80.9°	- 180 · 2°	-130·8°
	18	0·5517	25·8	-2·52	-59.1	- 95 · 2	-98·1
	18	0·5329	25·2	-2·86	-67.6	- 108 · 9	-94·1
	18	0·5013	25·25	-3·13	-78.8	- 126 · 9	-125·4

In the last column of the table are given the molecular rotatory powers obtained by Pope and Peachey (this vol., p. 1116) for lævotetrahydroquinaldine in the various solvents used; it is a very suggestive fact that the molecular rotatory power of the two homologous bases in benzene, acetone, and chloroform solution respectively are almost identical.

Leevotetrahydroparatoluquinaldine is nearly odourless, and does not become coloured on exposure to light; it is extremely soluble in the ordinary organic solvents, and was only obtained in good crystals from its solution in light petroleum.

$Lavotetrahydoparatoluquinaldine Hydrochloride, C_{11}H_{15}N,HCl+H_{2}O.$

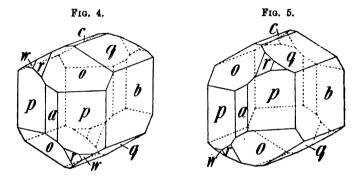
A solution of the base in excess of warm hydrochloric acid deposits, on cooling, levotetrahydroparatoluquinaldine hydrochloride in minute, colourless, monohydrated crystals which become anhydrous at 100° and melt at 194—196°. The anhydrous salt gave the following analytical results:

 $C_{11}H_{15}N,HCl$ requires $C=66\cdot83$; $H=8\cdot10$; $Cl=17\cdot92$ per cent.

1.6421 air-dried salt lost 0.1339 at 100°.

 $C_{10}H_{15}N$, $HCl + H_2O$ requires $H_2O = 8.35$ per cent.

A cold solution of the salt in hydrochloric acid deposits on spontaneous evaporation large, highly lustrous, transparent crystals (Fig. 4) belonging to the orthorhombic system and showing sphenoidal hemihedrism.



The crystals are enantiomorphously related to those of dextrotetra-hydroparatoluquinaldine hydrochloride (Fig. 5). The pinacoid $b\{010\}$ is usually dominant, and the prism $p\{110\}$ is the next largest form present. The pinacoids $a\{100\}$ and $c\{001\}$ and the dome $r\{101\}$ are always small but well-developed; the hemipyramid $o+\{111\}$ is large, whilst the faces of the complementary form, $w-\{111\}$ are present as minute, triangular replacements. The form $q\{011\}$ is always represented by large, lustrous faces; the crystals give very good results on measurement.

Crystalline system.—Orthorhombic. Sphenoidal hemihedrism.

a:b:c=0.8165:1:0.5703.

Forms observed on crystals of lævotetrahydroparatoluquinaldine hydrochloride.— $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r\{101\}$, $o+\{111\}$, and $w-\{111\}$.

Forms observed on crystals of dextrotetrahydroparatoluquinaldine hydrochloride.— $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r\{101\}$, $o - \{111\}$, and $w + \{111\}$.

The following angular measurements were made on crystals of both the lawo- and the dextro-isomeride:

Angle.	Number of observatious.	Limits.	Mean.	Calculated.
$ap = 100:110$ $bp = 010:110$ $pp = 110:1\overline{10}$ $bq = 010:011$ $cq = 001:0\overline{11}$ $ac = 100:001$ $co = 001:111$ $po = 110:1\overline{11}$ $po = 110:1\overline{11}$ $po = 110:1\overline{11}$ $po = 110:1\overline{11}$ $po = 110:1\overline{11}$ $po = 110:1\overline{11}$ $po = 110:1\overline{11}$	26 45 20 39 15 82 13 27 18 10 39	38°42′— 39°40′ 50 17 — 51 14 78 0 — 78 56 59 49 — 60 41 29 17 — 30 5 58 44 — 59 47 89 47 — 90 15 41 39 — 42 30 47 25 — 48 12 131 49 — 132 16 83 42 — 84 29 58 27 — 59 0 30 58 — 31 33	89°13′ 50 46 78 27 60 15 29 43 59 20 90 0 42 8 47 56 132 1 84 6 58 45 31 15	39°14′ 78 28 60 18 29 42 59 28 90 0 42 2 47 58 132 2 84 5 58 45 31 15
$ow = 111 : \overline{1}11$ $bo = 010 : 111$ $ow = 111 : 1\overline{1}1$ $bw = 010 : 1\overline{1}1$ $or = 111 : 101$ $ar = 100 : 101$	14 48 35 18 24 32	62 7 — 62 51 64 32 — 65 12 49 44 — 50 21 114 38 —115 39 24 40 — 25 27 54 51 — 55 19	62 29 64 56 80" 50 6 115 4 25 4 55 6	62 29

After melting on a microscope slide, the anhydrous salt crystallises readily from centres whilst still hot in long, individual flakes enclosing long, pear-shaped, vacuous holes; the flakes extinguish parallel to their direction of growth and crack across considerably during cooling. The pieces usually lie perpendicularly to the bisectrix of a large optic axial angle of positive double refraction; the optic axes emerge outside the microscope field. At the ordinary temperature, the substance solidifies very slowly to a finely grained mass showing aggregate polarisation.

The following determinations of the rotation constants were made: 0.5583 gram of the air-dried salt, having the composition $C_{11}H_{15}N,HCl+H_2O$, made up to 25.3 c.c. with water at 19° , gave the value $a_D-2.86^\circ$ in a 200 mm. tube, whence $[a]_D-64.7^\circ$ and $[M]_D-139.7^\circ$. 0.4803 gram of salt dried at 100° , having the composition $C_{11}H_{16}N,HCl$, made up to 25.2 c.c. with water at 19° , gave the value $a_D-2.69^\circ$ in a 200 mm. tube, whence $[a]_D-70.6^\circ$ and $[M]_D-139.4^\circ$. The molecular rotatory power of lavotetrahydroparatoluquinaldine hydrochloride, namely, $[M]_D-139.5^\circ$, is considerably greater than that of lavotetrahydroquinaldine hydrochloride, namely, $[M]_D-121.7^\circ$ (compare Pope and Peachey, this vol., p. 1072).

Benzoyllævotetrahydroparatoluquinaldine, C11 H14 N·CO·C6 H5.

Levotetrahydroparatoluquinaldine hydrochloride is converted into its benzoyl derivative by agitation with warm soda and benzoic chloride; the oily product crystallises on standing, and is purified by repeated crystallisation from hot acetone. It crystallises in long, colourless needles melting at $100-101^{\circ}$, and is fairly soluble in hot alcohol, acetone, or ethylic acetate; attempts to obtain crystals suitable for goniometrical measurement were unsuccessful. The following analytical results were obtained:

Its specific rotatory power was determined in a benzene solution containing 0.5150 gram in 25·1 c.c. at 18°; the rotatory power was found to be $a_{\rm D}+9.39^{\circ}$ in a 200 mm. tube, whence $[a]_{\rm D}+229^{\circ}$ and $[M]_{\rm D}+606^{\circ}$. Although the molecular rotatory power of benzoyl-lævotetrahydroparatoluquinaldine, $[M]_{\rm D}+606^{\circ}$, is rather less than that of benzoyllævotetrahydroquinaldine, namely, $[M]_{\rm D}+630^{\circ}$, yet both derivatives of the lævorotatory bases are highly dextrorotatory; the following table gives the molecular rotatory powers $[M]_{\rm D}$ of the two sets of compounds:

	$C_{10}H_{18}N$.	C ₁₁ H ₁₅ N.
Z-Base in benzene	- 130·3°	- 130·2°
	- 121.7	- 139.5
Hydrochloride of l-base	+680	+606

II. DEXTROTETRAHYDROPARATOLUQUINALDINE.

The liquors remaining after the deposition of lævotetrahydroparatoluquinaldine dextrobromocamphorsulphonate yielded a separation of dextro-base containing some of its lævo-isomeride when treated with soda; the base, with the addition of a molecular proportion of dextro-camphorsulphonic acid, was dissolved in hot ethylic acetate, and on cooling a copious crystalline separation occurred. After several recrystallisations from boiling acetone, this material—dextrotetrahydroparatoluquinaldine dextrocamphorsulphonate—was obtained in colourless needles melting at 194—196°. The salt is sparingly soluble in ethylic acetate or acetone but very soluble in water; on treating its aqueous solution with soda, a product melting at 37—40° was obtained.

so that evidently it did not consist wholly of the dextro-base (compare Pope and Peachey, this vol., p. 1078).

Dextrotetrahydroparatoluquinaldine Hydrochloride, $C_{11}H_{15}N,HCl+H_2O$.

The whole of the impure dextro-base was converted into hydrochloride and the salt repeatedly crystallised from boiling acetone containing a little water; the solution was allowed to become supersaturated to a considerable extent, and crystallisation induced by scratching in order, if possible, to avoid the difficulty met with in isolating dextrotetrahydroquinaldine hydrochloride (this vol., p. 1079). As the result of a series of crystallisations, pure dextrotetrahydroparatoluquinaldine hydrochloride was obtained as a colourless, crystalline powder melting at 194—196°.

On spontaneous evaporation of its hydrochloric acid solution, the salt was obtained in large, sphenoidally hemihedral orthorhombic crystals, of which measurements are given above (p. 1098).

The following analytical results were obtained with the anhydrous salt:

0.1335 gave 0.3261 CO₂ and 0.0988 H₂O. C = 66.62; H = 8.22.

0.1248 , 0.3054 CO_2 , 0.0931 H_2O . C = 66.73; H = 8.29.

0.2709 , 0.1982 AgCl. Cl = 18.11.

 $C_{11}H_{15}N$, HCl requires C = 66.83; H = 8.10; Cl = 17.92 per cent.

1.7730 air-dried salt lost $0.1500 \text{ H}_2\text{O}$ at 100° .

 $C_{11}H_{15}N,HCl+H_2O$ requires $H_2O=8.35$ per cent.

The value $a_D + 2.86^\circ$ was observed in a 200 mm. tube with an aqueous solution containing 0.5125 gram of the anhydrous salt in 25.2 c.c. at 18°, whence $[a]_D + 70.3^\circ$ and $[M]_D + 138.9^\circ$, numbers agreeing closely with those obtained for the optical antipodes.

Dextrotetrahydroparatoluquinaldine, $C_{11}H_{15}N$.

On adding soda to an aqueous solution of the hydrochloride, the base separates as an oil which immediately solidifies to a white, crystalline mass; when crystallised by the spontaneous evaporation of its solution in light petroleum boiling at 20—50°, it is obtained in hemimorphic, monosymmetric prisms melting at 52—53°, of which goniometric measurements are given above (p. 1096). The following analytical results were obtained:

0.1168 gave 0.3503 CO₂ and 0.1020 H₂O. C=81.80; H=9.70.

0.1236 , 0.3701 CO_2 , $0.1074 \text{ H}_2^{-}\text{O}$. C = 81.66; H = 9.66.

 $C_{11}H_{16}N$ requires C=81.98; H=9.32 per cent. VOL. LXXV

A solution of 0.4924 gram, made up to 25.3 c.c. with benzene at 19°, gave $a_D + 3.14^\circ$ in a 200 mm. tube, whence $[a]_D + 80.7^\circ$ and $[M]_D + 129.9^\circ$; the corresponding numbers obtained for the laworotatory base were $[a]_D - 80.9^\circ$ and $[M]_D - 130.2^\circ$.

INACTIVE TETBAHYDROPARATOLUQUINALDINE.

Externally compensated tetrahydroparatoluquinaldine was described by Doebner and von Miller (Ber., 1883, 16, 2464) as an almost colourless oil, but we found, on treating its hydrochloride with soda in aqueous solution, that it separates as a colourless oil which readily solidifies at the ordinary temperature and is but slightly liable to superfusion; it would seem therefore that Doebner and von Miller never obtained the base in a pure state.

After purification by crystallisation from light petroleum boiling at 25—30°, the base is obtained as a white, granular, crystalline mass, melting at 31—32°. The following analytical results were obtained:

```
0.1203 gave 0.3602 CO<sub>2</sub> and 0.1042 H<sub>2</sub>O. C=81.65; H=9.63.
0.1189 ,, 0.3563 CO<sub>2</sub> ,, 0.1024 H<sub>2</sub>O. C=81.72; H=9.57.
C_{11}H_{15}N requires C=81.98; H=9.32 per cent.
```

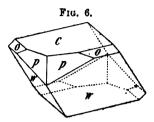
The base could not be obtained in measurable crystals by crystallisation from any of the ordinary organic solvents; it is distinctly more soluble in light petroleum than are its active components. After melting on a microscope slide, it solidifies readily in six-sided, monosymmetric plates, the top face being a(100); the forms $c\{001\}$ and $q\{011\}$ are also present. The plane angle $011:01\overline{1}$ is about 112° , the optic axial plane is the plane of symmetry, and the positive bisectrix and one optic axis emerge through a(100). This similarity between the crystalline forms of the active and inactive bases, and the greater solubility of the latter in light petroleum, suggest that the externally compensated base is either pseudoracemic or a mere mixture of the two antipodes; this question will be subsequently investigated.

Racemic Tetrahydroparatoluquinaldine Hydrochloride, C11H15N, HCL

After reducing paratoluquinaldine by Doebner and von Miller's method, racemic tetrahydroparatoluquinaldine hydrochloride is obtained as a white, crystalline powder which, after crystallisation from alcohol, melts at 180—183°, and unlike the optically active hydrochlorides is anhydrous. On analysis, the following results were obtained:

```
0.1147 gave 0.2808 CO<sub>2</sub> and 0.0863 H<sub>2</sub>O. C=66.77; H=8.36. 0.1193 , 0.2917 CO<sub>2</sub> , 0.0886 H<sub>2</sub>O. C=66.68; H=8.25. 0.2613 , 0.1907 AgOl. Ci=18.07. C<sub>11</sub>H<sub>18</sub>N,HCl requires C=66.83; H=8.10; Cl=17.92 per cent.
```

It is very soluble in water, less so in alcohol, and only sparingly soluble in boiling acetone. On spontaneous evaporation of its solution in dilute hydrochloric acid, it separates in large, colourless, transparent, monosymmetric prisms of calcite-like lustre (Fig. 6). The pyramid w{111} is usually dominant, and the pinacoid $c\{001\}$ is well developed; the forms



o{111} and p{210} are generally small, but their faces give good results on measurement. The extinction in $w\{111\}$ makes about an angle of 10° with the edge cw, and there is a perfect cleavage parallel to w[111]; the bisectrix of negative double refraction and one optic axis are observed to emerge through a cleavage plate, so that the plane of symmetry is the optic axial plane.

Crystalline system.—Monosymmetric.

$$a:b:c=1.4140:1:1.0601.$$

$$\beta = 81^{\circ} 5'$$
.

Forms observed.— $c\{001\}$, $p\{210\}$, $o\{111\}$, $w\{\bar{1}11\}$.

The following angular measurements were obtained:

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
co =001:111 ow =111:11Ī cw =001:Ī11 pp =210:2Ī0 cp =001:210 cp =001:210 pw =210:11Ī oo =111:ĪĪ1 ww = Ī11:ĪТ1	26 29 48 38 44 86 8 16 19	48°45′—50° 1′ 74 57 —76 14 54 46 —56 0 69 27 —70 12 82 16 —83 27 96 45 —98 5 44 56 —45 59 75 38 —77 42 83 45 —85 17 94 87 —96 1	49°24′ 75 48 55 26 69 52 82 42 97 29 45 23 76 81 84 36 95 27	49°58' 75 36 — — 97 18 45 44 76 2 84 30 95 30

After melting on a microscope slide, the racemic hydrochloride solidifies more readily at the ordinary temperature than its active com-It solidifies quite readily whilst hot from centres in long needles containing irregularly-shaped vacuous bubbles. Many of the Digitized by 200910

fragments are of the same shape as cleavage flakes of the crystals deposited from solution, and exhibit identical optical properties; it is therefore proved that the molten mass solidifies as a racemic compound.

Racemic Benzoyltetrahydroparatoluquinaldine, C11H14N·CO·C6H5.

On treating the racemic hydrochloride with soda and benzoic chloride, the benzoyl derivative is obtained with ease, and after recrystallisation from acetone forms long, colourless needles melting at 103—105°; it is sparingly soluble in cold alcohol, acetone, or ethylic acetate, but fairly readily soluble in the hot solvents. The following analytical results were obtained:

0.1286 gave 0.3842 CO₂ and 0.0852 H₂O. C=81.47; H=7.36. 0.1339 ,, 0.3994 CO₂ ,, 0.0877 H₂O. C=81.35; H=7.28.
$$C_{18}H_{19}ON$$
 requires C=81.51; H=7.17 per cent.

On spontaneous evaporation of its solution in acctone, the benzoyl derivative is deposited in large, colourless, transparent, monosymmetric prisms (Fig. 7); the pinacoid $b\{010\}$ is dominant, and the form



 $c\{001\}$ is the smallest present. Since none but pinacoid forms were observed, the axial ratios could not be determined; all the faces are of conchoidal character, so that the measurements are not very good.

Crystalline system.—Monosymmetric.

$$a:b:c=?$$

$$\beta = 84^{\circ} 11'$$
.

Forms observed.— $a\{100\}$, $b\{010\}$, and $c\{001\}$.

The following angular measurements were obtained:

Number of observations.			Calculated.	
24	82°17′—86°20′	84°11′		
18	88 29 91 55	89 48	90°0′	
21	88 40 —91 16	89 57	90 0	
C	24 18	24 82°17′—86°20′ 18 88 29 —91 55	24 82°17′—86°20′ 84°11′ 18 88 29 —91 55 89 48	

There is a perfect cleavage on $a\{100\}$ and the extinction in $b\{010\}$ makes about 15° with the edge ab. The optic axial plane is perpendicular to the plane of symmetry, and the acute optic axial bisectrix emerges through $c\{001\}$; the optic axial angle is fairly large, and the angle for blue is greater than that for red light.

Our thanks are due to the Government Grant Fund Committee of the Royal Society and to the Research Fund Committee of the Chemical Society for grants enabling the purchase of apparatus and material used in this work.

GOLDSMITHS' INSTITUTE, NEW CROSS, S.E.

CX.—The Application of Powerful Optically Active Acids to the Resolution of Externally Compensated Basic Substances. Resolution of Racemic Camphoroxime.

By WILLIAM JACKSON POPE.

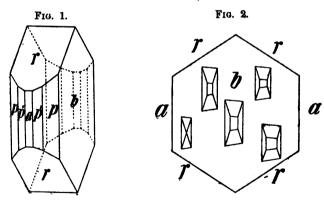
ALTHOUGH tartaric acid may be used in separating the constituents of inactive mixtures of powerful optically active bases, being a weak acid it cannot be successfully used in conjunction with weak bases. In the present communication, it is shown that the separation is readily effected, even in the case of so weak a base as camphoroxime, by means of the strong acid Reychler has prepared by sulphonating camphor. This acid was chosen instead of dextro-a-bromocamphorsulphonic acid, because it is not so hygroscopic as the latter, and it is possible, therefore, to avoid access of water in working with it.

Racemic camphoroxime (60 grams) and carefully purified dextrocamphorsulphonic acid (90 grams) are dissolved in a small quantity of boiling acetone; as the liquid cools, a crystalline, but not homogeneous, product separates, of which further quantities may be obtained from the mother liquor. The whole of the crystalline material produced in the operation is then fractionally crystallised from boiling ether in a series of beakers, the mother liquors going in one direction through the series, and the crystalline deposits in the other. As the systematic fractionation proceeds, it is noticed that the deposits become more sparingly soluble in the ether, and ultimately two pure products are isolated; the less soluble substance is dextrocamphoroxime* dextrocamphorsulphonate, and the more soluble is levocamphoroxime dextrocamphorsulphonate.

^{*} The name dextrocamphoroxime is retained for the laworotatory oxime obtained from dextrocamphor.

$\begin{array}{c} \textit{Dextrocamphoroxime} \quad \textit{Dextrocamphorsulphonate}, \\ \text{$C_{10}H_{16}N\cdot OH, C_{10}H_{15}O\cdot SO_3H+H_2O}. \end{array}$

Dextrocamphoroxime dextrocamphorsulphonate separates in long, colourless, transparent needles from its ethereal solution; it is very soluble in alcohol, benzene, acetic acid, chloroform, and most other organic solvents, and the solutions on evaporation usually become syrupy, and crystallise with difficulty. It is very sparingly soluble in ethylic acetate or ether and is precipitated as an indistinctly crystalline mass on adding light petroleum to its solution in benzene. On spontaneous evaporation of its cold acetone solution, it separates in magnificent, lustrous, transparent, orthorhombic tablets, sometimes 30 mm. in length (Fig. 1). The pinacoid b{010} is predominant, and the dome $r\{101\}$ is the next best form represented; the form $p\{110\}$ is larger than $p'\{210\}$, and both are larger than the pinacoid $a\{100\}$. the forms observed give fairly good results on measurement. The crystals exhibit no external signs of hemihedral structure, but there is a very perfect cleavage parallel to b{010}, and on etching cleavage surfaces with benzene, etch-figures of the appearance represented in Fig. 2 are formed; two of the bounding sides of these figures appear



parallel to each other and to the axis-c, but the other two sides seem to be not parallel, and to make different angles with the axis-a. It is very difficult to be absolutely sure of this, but the etch-figures seem to indicate the sphenoidally hemihedral crystalline structure of the material.

Crystalline system.—Orthorhombic: Sphenoidal hemihedrism.

a:b:c=1.2024:1:0.8943.

Forms observed,— $a\{100\}$, $b\{010\}$, $p\{110\}$, $p'\{210\}$, $r\{101\}$.

Angle.	Number of measurements.	Limits.	Mean.	Calculated.
$bp = 010:110$ $pp' = 110:210$ $ap' = 100:210$ $p'p' = 210:2\overline{10}$ $ar = 100:101$	42 17 19 14 28	39°16′—40°18′ 18 54 —19 34 80 45 —31 26 61 30 —62 28 52 59 —54 1	39°45′ 19 12 31 3 61 59 53 29	19°14′ 31 1 62 2 53 21·5
$rr = 101 : \overline{1}01$ pr = 110 : 101 p'r = 210 : 101	39 12 5	72 46 —73 35 67 1 —68 9 58 47 —59 34	73 17 67 38 59 11	67 84 59 14

The following angular measurements were obtained:

The acute bisectrix emerges perpendicularly through a cleavage plate; the optic axial plane is a(100) and the axis-b is the acute bisectrix. The optic axial angle is large, and the double refraction positive in sign. After melting on a microscope slide and cooling, the material crystallises very slowly; crystallisation may be started and caused to proceed fairly rapidly by cautiously warming the preparation. The crystallisation is very confused, but consists mainly of long needles, many of which lie perpendicularly to the acute bisectrix of a large optic axial angle; the double refraction is positive in sign, and this modification is crystallographically identical with the crystals deposited from the acetone solution.

Dextrocamphoroxime dextrocamphorsulphonate has an odour of camphoroxime, and on exposure to air the percentage of sulphur gradually increases, owing to volatilisation of the oxime. The carefully purified material crystallised from acetone, powdered, and dried for a short time in the air, melted at 91—92°, and gave the following results on analysis:

```
0.1785 gave 0.3778 CO<sub>2</sub> and 0.1341 H<sub>2</sub>O. C = 57.72; H = 8.34.
```

0·1964 ,, 0·4140 CO₂ ,, 0·1494
$$H_2O$$
. $C = 57.49$; $H = 8.46$. 0·3528 .. 0·2113 BaSO.. $S = 8.29$.

$$\begin{array}{c} {\rm C_{20}H_{38}O_5NS+H_2O\ requires\ C=57.55\ ;\ H=8.39\ ;\ S=7.67\ ;} \\ {\rm C_{10}H_{15}O.SO_3H=55.63\ per\ cent.} \end{array}$$

The rotation constants of the salt were determined in absolute alcohol solution; 0.4377 gram, made up to 25 c.c., gave $a_D + 0.15^{\circ}$ in a 200 mm. tube at 21°; whence $[a]_D + 4.3^{\circ}$ and $[M]_D + 17.9^{\circ}$.

^{0.3528 ,, 0.2113} BaSO₄. S = 8.29. 1.1331 required 27.1 c.c. N/10 NaHO for neutralisation. $C_{10}H_{\delta}O \cdot SO_{g}H = 55.49$.

Lavocamphoroxime Dextrocamphoreulphonate, $C_{10}H_{16}N \cdot OH, C_{10}H_{15}O \cdot SO_8H + H_2O.$

Leevocamphoroxime dextrocamphorsulphonate is even more soluble in the ordinary organic solvents than the salt of dextrocamphoroxime, and the solutions in alcohol, benzene, and acetic acid become syrupy on evaporation in the air. It crystallises on spontaneous evaporation of its solutions in ether, ethylic acetate, and acetone in tiny needles melting at 90-91°, and attempts to obtain measurable crystals were unsuccessful. The small crystals are remarkably similar to those of dextrocamphoroxime dextrocamphorsulphonate in shape and crystallographic properties; they are flattened upon a six-sided face, b(010), and the acute bisectrix emerges nearly perpendicularly through this face. The double refraction is positive in sign, and the optic axial angle is large; the plane angle between the two faces corresponding to (101) and (101) on the salt of dextrocamphoroxime was measured as 111-117°, as against 107° on the latter compound. After melting the substance on a microscope slide under a cover slip, it crystallises very slowly at the ordinary temperature from centres in long, flattened needles; these are crystallographically identical with the crystals deposited from solution, and their formation is hastened by gently warming the plate.

The following analytical results, obtained with material crystallised from acetone, powdered and dried in the air, show that the salt has the same composition as that from dextrocamphoroxime:

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0.1865 gave 0.3937 CO<sub>2</sub> and 0.1407 H<sub>2</sub>O. C = 57.57; H = 8.38. 0.2197 , 0.4637 CO<sub>2</sub> , 0.1663 H<sub>2</sub>O. C = 57.56; H = 8.41.
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0.3804 , 0.2371 BaSO₄. S = 8.54.

1.2285 required 29.4 c.c. N/10 NaHOfor neutralisation. $C_{10}H_{18}O\cdot SO_8H$ = 55.51.

$$C_{20}H_{33}O_5NS + H_2O$$
 requires $C = 57.55$; $H = 8.39$; $S = 7.67$; $C_{10}H_{16}O\cdot SO_3H = 55.63$ per cent.

Although it seems to be proved by the analytical results given above that these two salts contain water of crystallisation, yet they are both decomposed on addition of water, with separation of the corresponding camphoroxime. In order to identify these, the salts were treated with water, when flocculent precipitates of the camphoroximes separated; the solutions were just neutralised with ammonia and the precipitates filtered off, washed, dried, and crystallised from hot alcohol.

0.5765 gram of the oxime obtained from dextrocamphoroxime dextrocamphorsulphonate, made up to 25.2 c.c. with absolute alcohol at 21°, gave $a_D - 1.89^\circ$ in a 200 mm. tube; whence $[a]_p - 41.3^\circ$, proving the material to be dextrocamphoroxime,

0.5870 gram of the oxime prepared from lævocamphoroxime dextrocamphorsulphonate, made up to 25.1 c.c. with absolute alcohol at 22.5° , gave $a_D + 1.95^{\circ}$ in a 200 mm. tube; whence $[a]_D + 41.7^{\circ}$, proving the substance to be lævocamphoroxime.

A consideration of the molecular rotatory powers of dextro- and levo-camphoroxime dextrocamphorsulphonate suggests very strongly that these salts are wholly dissociated in alcoholic solution; if such were the case, the difference between the molecular rotatory powers of the two compounds should be twice the molecular rotatory power of camphoroxime in alcoholic solution. In fact, the numbers are $166.8 - 17.9 = 148.9 = 2 \times 74.4$, whereas the molecular rotatory power of active camphoroxime in alcoholic solution is 70° or 71°; the molecular rotatory powers, 70° and 74,° are equal within the rather wide limits of experimental error involved in dealing with these compounds. It might possibly be expected that other salts of the camphoroximes should similarly dissociate in alcoholic solution; Forster (Trans., 1897, 71, 1045) has given the specific rotatory power of dextrocamphoroxime hydrobromide as $[a]_n - 35.8^\circ$, whence the molecular rotation may be calculated as [M]_D - 88.7°, which, if the compound dissociated in the alcoholic solution, should be equal to the molecular rotatory power of dextrocamphoroxime, namely, $[M]_p - 71^\circ$.

A consideration of the foregoing work will make it obvious that we are for the first time in possession of a method for resolving externally compensated oximes into their optically active components, and that it is therefore now possible, in many cases, to separate racemic ketones and aldehydes by purely chemical methods. Many important applications of the new method are evident, such, for instance, as to the elucidation of the constitution of oximes. No chemical method affording direct evidence has yet been devised for judging between Hantzsch and Werner's and rival hypotheses as to the constitution of the oximes. According to the one view, however,

N-phenylbenzaldoxime has the constitution CHPh $<_{\mathrm{NPh}}^{\mathrm{Q}}$, and hence contains an asymmetric carbon atom, whilst, according to other views, the constitution contains no asymmetric carbon atom, a distinction which may admit of recognition in this, or similar cases, by the use of a method like that now described. Experiments are in progress with this object in view.

My hearty thanks are due to the Research Fund Committee of the Chemical Society for a grant defraying the cost of the materials used in this work.

Goldsmiths' Institute, New Cross.



CXI.—Homogeneity of Dextrolævo-a-phenethylamine Dextrocamphorsulphonate.

By WILLIAM JACKSON POPE AND ALFRED WILLIAM HARVEY.

LEVO-a-PHENETHYLAMINE was isolated by Lovén (Ber., 1896, 29, 2313) in an impure state by fractionally crystallising the acid tartrates of the externally compensated base. In the hope of finding a method of obtaining the pure active bases in quantity, we mixed the inactive base with the corresponding weight of Reychler's dextrocamphorsulphonic acid in hot acetone solution. On cooling, a crystalline salt separated and was purified by crystallisation from acetone.

Dextrolævo-a-phenethylamine Dextrocamphorsulphonate, $C_6H_5 \cdot CH(CH_5) \cdot NH_2, C_{10}H_{15}O \cdot SO_5H$.

The salt is deposited from its cooling acetone solution in minute, colourless plates melting at 141—143°; the following analytical results were obtained:

0.1976 gave 0.4436 CO₂ and 0.1353 H₂O.
$$C = 61.22$$
; $H = 7.60$. $C_{18}H_{27}O_4NS$ requires $C = 61.19$; $H = 7.64$ per cent.

An aqueous solution containing 0.5079 gram in 25.1 c.c. at 19° gave $a_D + 0.59^\circ$ in a 200 mm. tube, whence $[a]_D + 14.6^\circ$ and $[M]_D + 51.5^\circ$. Since Pope and Peachey have shown (this vol., p. 1086) that the molecular rotatory power of ammonium dextrocamphorsulphonate is $[M]_D + 51.7^\circ$, it is evident that the salt now described belongs to the class of "partially racemic" substances discovered by Ladenburg (Ber., 1898, 31, 524).

The salt is very soluble in water, alcohol, or acetone, and on spontaneous evaporation the solutions become gummy and do not yield good crystals. The crystals deposited from hot acetone solutions are minute, rectangular plates having their corners replaced. They show straight extinction and the acute bisectrix of positive double refraction emerges perpendicularly through the large face of the plate; the optic axial angle is fairly large. After melting on a microscope slide, the liquid solidifies with great reluctance, depositing plates crystallographically identical with those obtained from the acetone solution.

Inactive a-Phenethylamine Platinochloride, (CHPhMe·NH₂)₂, H₂PtCl₆.

—Both the dextrocamphorsulphonate and the hydrochloride of the base

yield the same platinochloride; this salt is very soluble in acetone and crystallises from a mixture of acetone and ethylic acetate in golden-yellow scales melting at 213—214°. The following analytical results were obtained:

0.1623 gave 0.0488 Pt. Pt = 30.06. $C_{16}H_{24}NCl_{6}Pt$ requires Pt = 29.96 per cent.

Goldsmiths' Institute, New Cross.

CXII.—A Method for Discriminating between "Non-racemic" and "Racemic" Liquids.

By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY.

ALTHOUGH during the last few years Ladenburg has persistently endeavoured to demonstrate the existence of racemic liquids, most of the methods which he has used afford results which have no bearing upon the question at issue. Thus he found (Annalen, 1888, 247, 87) that on converting a mixture of dextro- and lævo-conine in unequal quantities fractionally into its compound with cadmium iodide, an alteration in the specific rotatory power of the mixture of bases could be effected, and concluded that this proved the racemic nature of inactive coniine, but Fischer pointed out (Ber., 1894, 27, 3224), and it follows from recent work of Kipping and Pope (this vol., p. 1119), that this fact has nothing to do with the racemic or non-racemic character of the liquid. Again, Ladenburg observed that on mixing dextro- and lævo-coniine a fall in temperature occurs, and attributed this to chemical change (Ber., 1895, 28, 164); he noted further that, although the density is not altered thereby, the refractive index increases notably. This result involves the remarkable conclusion, which Ladenburg does not draw, that the molecular refraction of "racemic" coniine is about 1 per cent. greater than that of its optically active components. Since so much depends upon the densities (compare Traube, Ber., 1896, 29, 1396), which are not given in the paper referred to, judgment must be deferred; Ladenburg, however, years ago (Annalen, 1888, 247, 81) gave experimental numbers showing the density of active and inactive conline to be the same. A criticism of his latest method (Ber., 1899, 32, 1822) is to be found in the following paper (p. 1119).

Although the methods hitherto adopted in the study of externally compensated liquids are so unconvincing, yet it seems possible to devise a trustworthy method. We owe to the labours of Ramsay and Shields (Zeit. physikal. Chem., 1893, 12, 433) and others the know-

ledge that many liquid substances are associated, the physical molecules being aggregates of several chemical molecules; some classes of compounds, such as bases, are highly associated, whilst others. like the hydrocarbons, have, in general, association factors approximating to unity. In this question of association is to be found the cause of many facts relating to optical activity which are otherwise difficult to explain (compare also P. Frankland, this vol., p. 347). a highly associated substance be dissolved in a solvent, it is to be expected that it will break down into simpler molecules more or less completely, the extent to which this occurs depending upon the solvent and the concentration; but if a liquid already consisting of chemical molecules be dissolved in a solvent, it cannot undergo further dissociation.* Further, if in any case it is possible for a solvent to cause an increase in the association factor of an already associated solute as suggested by Frankland (this vol., p. 363), this is an unlikely contingency when the pure solute has an association factor approximating to unity. Since an optically active substance necessarily has different rotation constants according as it is associated to different degrees, we must expect to find that the specific rotatory power of substances having high association factors in the pure liquid state varies considerably with change of solvent and of concentration, whilst those substances having in the pure liquid state association factors approximating to unity would in solution have specific rotatory powers but slightly dependent on the solvent and the concentration. An examination of the rather meagre data available, shows this conclusion to be appreciably in accord with the facts, substances which from their nature should have high association factors exhibiting very different specific rotatory powers as the solvent is changed, whilst those which should be nearly monomolecular vary but slightly in specific rotatory power in like circumstances. Results are given in the present paper showing that, in the case of levotetrahydroquinaldine, [a] varies from -45.9° to -117.9° in various solvents, whilst the specific rotatory power of lavopinene varies in different solvents between $[a]_{n} - 33^{\circ}$ and -42° . Although we have no direct information respecting the association factors of these two substances in the pure state, yet from the fact that Traube (Ber., 1897, 30, 265) gives the association factors of aniline, pyridine, quinoline, and piperidine as 1.35, 1.75, 1.40, and 1.62 respectively at the ordinary temperature, and the association factors of the aliphatic hydrocarbons and the higher homologues of benzene as unity, it may be judged that levopinene is monomolecular, whilst the association factor of levotetrahydroquinaldine is about 1.5.

^{*} The question of electrolytic or of hydrolytic dissociation is naturally not referred to here,

In a preceding paper (p. 1066), we have elaborated a method by which at least one optically active component of an externally compensated base can be prepared in quantity, and in a state closely approaching purity. We purpose continuing this work, supplementing it with a careful comparison of the active and inactive liquid bases; in the present paper we give the results obtained with the tetrahydroquinaldines: results which justify us in definitely concluding that, at the ordinary temperature, dextro- and lævo-tetrahydroquinaldine exist in the same state of molecular aggregation, whether separate or mixed, and therefore do not combine to form a liquid racemic compound.

A considerable number of data respecting the densities of optically active and externally compensated liquids has been collected, but the only available accurate values we have been able to find are those given by Ladenburg (Annalen, 1888, 247, 81) in his classical work on coniine; he finds that the densities of lavo- and inactive coniine at 0°/0°, are 0.8625 and 0.8626 respectively, numbers identical within the limits of experimental error. Density determinations of the active and inactive alkylic glycerates have been given by Frankland and MacGregor (Trans., 1893, 63, 511); these data, and also those given by Schütz and Marckwald (Bor., 1896, 29, 52) for the valeric acids, allow of no conclusions being drawn as the experimental error is apparently large. Traube (Ber., 1896, 29, 1394) concludes from the densities of the active and inactive limonenes and carvones, that these substances are monomolecular, and that the inactive substances are merely mixtures; the density numbers used are, however, only very approximate.

Densities of Lavo- and Externally Compensated Tetrahydroquinaldine.

We obtained lævotetrahydroquinaldine in a highly purified condition by distilling its dextro-a-bromocamphorsulphonate (this vol., p. 1067) with soda in a current of steam, extracting the distillate with purified ether, and distilling off the ether on the water-bath; the residual oil is then repeatedly distilled under about 50 mm. pressure. Highly purified samples of externally compensated tetrahydroquinaldine have been prepared in a similar manner from the pure racemic hydrochloride (this vol., p. 1086). The densities were determined in a Sprengel tube holding about 5.4 c.c., with the following results:

Lavotetrahydroquinaldine.

- (1) Preparation B: d at $14.5^{\circ}/4^{\circ} = 1.02365$.
- (2) ,, A: ,, $18.5^{\circ}/4^{\circ} = 1.02046$.
- (3) ,, B: ,, $20\cdot2^{\circ}/4^{\circ}=1\cdot01914$.

Externally Compensated Tetrahydroquinaldins.

- (4) Preparation C: d at $14.5^{\circ}/4^{\circ} = 1.02362$.
- (5) , D: , $16.5^{\circ}/4^{\circ} = 1.02219$.
- (6) , D: , $18.0^{\circ}, 4^{\circ} = 1.02083$.
- (7) The density of a mixture of 2.8503 grams of lævotetrahydroquinaldine (preparation B) with 7.3455 grams of externally compensated tetrahydroquinaldine (preparation D) was found to be 1.01915 at $20.2^{\circ}/0^{\circ}$.

Four different preparations, A, B, C, and D, were used. An examination of the above seven determinations shows that within the limits of experimental error the density of all the samples is given by the expression, d at $t/4^\circ = 1.01930 + 0.00079$ (20 – t), so that the leevobase, the inactive base, and the mixture have the same density at the same temperature.

A dextrorotatory base and its lævorotatory antipodes necessarily have the same density under the same conditions; if both are associated and no chemical action occurs on admixture, it would be expected that no change in the association factor of either isomeride follows admixture. This latter condition can only be fulfilled if no alteration of density occurs; from the density determinations alone we must therefore conclude as highly probable that no alteration in the state of molecular aggregation occurs on mixing dextro- and lævo-tetrahydro-quinaldine.

Refraction Constants of Lavo- and Externally Compensated Tetrahydroquinaldine.

The refractive indices of lævo- and externally compensated tetrahydroquinaldine (preparations B and D) were determined for sodium and thallium light in a hollow glass prism of about 60° angle; the results are given in the following table, the molecular refractions,

 \mathfrak{M} , being calculated from the expression, $\mathfrak{M} = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$

Sample.	t.	Light.	n.	35.
Leevo- B	24°	Na	1.57050	47.50
Inactive D	22°	Tl Na	1·57724 1·57273	48·07 47·57
,, ,,	"	Tl	1.58184	48.19

The values for the D-line are probably more nearly accurate than those for the less luminous thallium flame; the molecular refractions, 25,

for the D-line are identical within the limits of experimental error. With the identity in density between the active and inactive bases there goes therefore an identity in refractive index at the same temperature and an identity in molecular refraction. By applying Traube's arguments (Ber., 1897, 30, 43) on the relation between the refraction constants and the association factor to the case of the tetrahydroquinaldines, it is seen that the association factors of the active and inactive bases are rigorously identical.

A perusal of Brühl's magnificent work on the refraction constants of nitrogen compounds furnishes material for an interesting comparison. In the appended table, we quote the values obtained by Brühl for the molecular refractions of N- and a-methylpiperidine (Zeit. physikal. Chem., 1895, 16, 222) and for N-methyltetrahydroquinoline (Zeit. physikal. Chem., 1897, 22, 395) together with the values which we now give for

Substance.	W.	Δ.	Observer.
N-methylpiperidine	31·74 31·32 48·02	0.42	Brühl.
a- ,, (lævo-) a- ,, (inactive).	47·50 47·57	0·52 0·45	W. J. P. and S. J. P.

the active and inactive a-methyltetrahydroquinoline and the differences, Δ , between the molecular refractions for the D-line of the N- and a-isomerides of both series. Attention should be drawn to the appreciable identity of the differences, Δ , between the molecular refractions of the secondary and tertiary polymethylenic bases.

Rotation Constants of Lævotetrahydroquinaldine.

The rotatory powers of the preparations A and B of lævotetrahydroquinaldine described above were determined in 100 mm. tubes for the D-line, and are very nearly the same.

Preparation.	t.	a _D .	[a] _p .	[M] ₂ .
A	20°	- 59·24°	- 58·12°	- 85·44°
	,,	- 59·32	- 58·20	- 85·56

The difference of 0.08° observed in a rotatory power of about 60° is probably mainly due to the impossibility of obtaining a pure D-line even by the use of a long dichromate tube as a screen. It is to be noted that our value for a_D at 20° , namely, 59.28° , is rather higher

than that given by Ladenburg (*Ber.*, 1894, 27, 77) for the dextro-base, namely, $a_0 + 58.35^{\circ}$.

Since it is certain that lævotetrahydroquinaldine is highly associated, we were not surprised to find that its specific rotatory power varies very considerably with the solvent. The rotations given in the following table refer to the preparation A, and the values of a_D were obtained in 200 mm. tubes, except in the case of the pure base, when a 100 mm. tube was used.

Solvent.	t.	w.	v.	a _D .	[a] _D .	[M] _∞
Piperidine	23.8	1.2382	15.00	- 7·58°	- 45·9°	- 67·5°
Ether	21.0	0.6338	25.24	- 2.55	- 50-8	-74.7
None	20.0		_	- 59.24	- 58.12	-85-44
Acetone	19.5	0.6415	25.24	- 3.22	- 63.3	- 93 ·1
quinoline	19.0	1.8957	10.10	-11.94	- 63.6	- 93.5
Ethylic alcohol	21.5	0.6454	25.20	-3.28	-64.0	-94-1
Methylic alcohol	19.5	0.6398	25 · 27	-8.80	-75.1	-110.4
Chloroform	21.5	0.6544	25.20	-4.43	-85.3	- 125.4
Benzene	21.0	0.6465	25-24	- 4.54	- 88.6	- 130·3
Carbon tetrachloride	21.5	0.6410	25.29	- 4.95	- 97.6	- 143.5
Acetic acid	21.0	0.6672	25.29	- 6.22	-117.9	- 178-3

A perusal of this table shows that as the solvent is changed the specific rotatory power of lævotetrahydroquinaldine alters from $[a]_D - 45 \cdot 9^\circ$ to $[a]_D - 117 \cdot 9^\circ$, and is therefore nearly three times as great in one solvent as in another; even disregarding the use of acetic acid as a solvent because of the chemical action which doubtless occurs, the fact remains that the specific rotatory power of the base in piperidine solution is less than one-half of what it is in carbon tetrachloride solution. These large variations in specific rotatory power with change of solvent can only be attributed to differences in the degree of association of the base in the various solutions.

Corroborative evidence of this can be obtained in two ways, by making use of the highly probable supposition that if an associated substance be dissolved in a solvent of identical association factor, the association factor of the solute will remain unaltered. We see from the table that on dissolving lævotetrahydroquinaldine in its isomeride, N-methyltetrahydroquinoline, the specific rotatory power increases by some 9 per cent.; although N-methyltetrahydroquinoline is isomeric with lævotetrahydroquinaldine, the latter is a secondary and the former a tertiary base, so that, structurally, the two substances differ considerably, and are not likely to have similar association factors. Tetrahydroquinaldine, and both are secondary bases in every way

closely resembling each other; it is therefore, *d priori*, highly probable that they have almost the same association factor. Further, it is to be noted that tetrahydroquinoline contains no asymmetric carbon atom. The rotation constants of the optically active base were determined in the lower homologue as solvent with the following results:

Solvent.	t.	1 0.	٧.	a _p in 1 dcm.	[a] _D .	[M] _D .
Tetrahydroquinoline	24 ·2°	1.0647	15.0	- 4·18°	- 58·9°	-86.6

In accordance with our expectations, the specific rotatory power of the base in this solvent (-58.9°) is almost identical with the specific rotatory power in the pure liquid state (-58.12°) , because the association factor remains almost unchanged.

Again, the determinations of the densities and refraction constants of levo- and externally compensated tetrahydroquinaldine indicate with great probability that the association factor is the same in both. If any combination existed between the dextro- and lævo-isomerides in the externally compensated base this would be impossible. optical antipodes are quite indifferent one to the other in the mixture, we should find the specific rotatory power of the lævo-base, dissolved in the externally compensated mixture as solvent, absolutely identical with the specific rotation of the pure liquid levo-base. If, however, the two antipodes are not quite mutually indifferent, the association factor would change on admixture and lævotetrahydroquinaldine could not have the same specific rotatory power when dissolved in the externally compensated base as solvent as when solvent-free. determination made with the mixture used in the density determinations, shows in the most conclusive manner possible that the former alternative is the true one:

w lævo-base.	w inac. base.	t.	d _{1/0°} .	a _D .	[a] _D .	[M]».
2.8508	7 -8455	20.2	1 01915	-16.28°	- 58·04°	- 85·29°

The specific rotatory power of lævotetrahydroquinaldine, per se, is $[a]_D - 58\cdot12^\circ$, whilst when dissolved in the externally compensated base the specific rotatory power has an identical value, namely, $[a]_D - 58\cdot02^\circ$.

It remains to be added that externally compensated tetrahydroquinaldine is the best example of a physically perfect liquid solution to VOL. LXXV.

which attention has yet been drawn—of a solution, namely, the physical properties of which are proportional means of those of the constituents.

Although it would appear that the variations in specific rotatory power of a substance dissolved in various chemically inert solvents are due mainly to changes in the association factor of the solute, this does not preclude the solvent from exerting a specific action upon the rotation constants quite apart from its influence upon the association factor. It would seem, however, that such a specific action is not exerted upon an active substance by the mixture of the two antipodes; this is evident from the fact that the specific rotatory powers of lævotetrahydroquinaldine and of lævopinene respectively are the same in the solvent free state as in solutions in which the externally compensated substance is used as solvent.

Solvent.	$\begin{bmatrix} a \end{bmatrix}_{\mathbf{D}}$. $c=2$.	[a] _B . c=4.	$\begin{array}{c} [\alpha]_{b}, \\ c = 12. \end{array}$
Methylic alcohol Ethylic alcohol Ethylic alcohol Ether Piperidine Benzene Acetone Ethylic acetate Carbon tetrachloride Acetic acid Chloroform	- 33·3° - 34·8 - 34·9 - 35·5 - 37·5 - 38·8 - 39·2 - 39·5 - 41·7 - 41·5	- 37·3° - 38·6 - 37·5 - 37·6 - 39·1 - 39·5 - 39·6 - 39·6 - 39·6 - 41·7	- 38·3° - 38·7 - 38·1 - 37·6 - 39·2 - 39·4 - 39·4 - 40·7 - 40·4

The change of specific rotatory power of a practically monomolecular substance like lævopinene, such as is observed when the solvent and concentration are altered, may be due to a specific action of the solvent apart from its effect upon the association factor of the solute; there is, indeed, evidence supporting the view that combination between the solute and solvent sometimes occurs in similar cases. The above table gives the specific rotatory powers in various organic solvents of a sample of lævopinene having $[\alpha]_D - 36.97^\circ$ at 21.2° when solvent free. The numbers obtained in the dilute solutions (c=2) are probably con-

c.	[a] _D at 21.2.	о.	[a], at 21.2°.
2	- 36·85°	40	- 36·97°
	- 36·87	50	- 36·98
8	-86·97	60	- 36·96
10	-87·00	70	- 87·00
12	- 86·95	80	- 36·97
20	- 86·98	90	- 86·94
80	- 86.99	100	- 86.97

siderably affected by experimental error. The table shows that the specific rotatory power of lævopinene varies in different solvents, but to a minute extent compared with the variation in specific rotatory power of lævotetrahydroquinaldine in different solvents. A series of determinations of the specific rotatory power of lævopinene dissolved in a carefully purified sample of externally compensated pinene was also made, and the results, given in the last table, contrast very strongly with those obtained with solvents other than inactive pinene.

The results obtained with the pinenes point to the same conclusion as do those with tetrahydroquinaldine, namely, that the two optical antipodes, when mixed together, are wholly without mutual influence, and that consequently there is no question of the two substances combining to form a racemic compound.

Our thanks are due to the Government Grant Committee of the Royal Society and to the Research Fund Committee of the Chemical Society for grants defraying the cost of apparatus and materials used in the above work.

Goldsmiths' Institute, New Cross.

CXIII.—The Characterisation of "Racemic" Liquids.

By Frederic Stanley Kipping and William Jackson Pope.

In a paper published early this year (this vol., p. 36), we proved that Ladenburg's general method for distinguishing between a racemic substance and a mixture of enantiomorphously related compounds (Ber., 1894, 27, 3065) is fallacious and cannot afford the criterion desired. Shortly afterwards, in a reply communicated to this Society (this vol., p. 466), Ladenburg, after admitting the justice of our criticisms, gave what he described as a "different form" to his previous statement of the method in question, but, as was pointed out by one of us at the time (Proc., 1899, 15, 73), the alteration in form was so profound that the new statement had no principle in common with the original one.

This new method, which was also described in a German version of the paper (Ber., 1899, 32, 864)—where it appeared as a spontaneous effort on the part of its author—consists in determining the solubility of the externally compensated substance with, and without, the addition of a small proportion of one of its optically active components; if the solubilities are different, then the substance is racemic, whilst, if they are the same, it is a mere mixture of the two enantiomorphs.

This method, so far as it is applied to crystalline substances, is, except

in isolated cases, perfectly valid, and is merely the logical outcome of Kenrick's work (Ber., 1897, 30, 1749) and our own (loc. cit.). Recently, however, Ladenburg has attempted to apply it to externally compensated liquids with the object of ascertaining whether they are racemic or mere mixtures (Ber., 1899, 32, 1822); and in some of these experiments, instead of determining the solubility of the externally compensated substance alone and in admixture with a small proportion of one of its optically active components, he adopts the better and more convenient plan of examining polarimetrically the solutions obtained in the two cases. He takes, for example, an optically inactive mixture of d- and l-limonene, shakes it with dilute alcohol insufficient to dissolve the whole, then adds a little d-limonene, and shakes again; on subsequently examining the alcoholic solution, he finds that it is optically inactive, and so he concludes that d- and l-limonene do not form a racemic liquid at the ordinary temperature.

Now the results obtained by such an application of the method afford no evidence whatever of the non-racemic nature or otherwise of the externally compensated liquid, and consequently the conclusions which Ladenburg draws from them have not the slightest value. The method is valid with crystalline substances, because in the case of a non-racemic mixture of optical antipodes two solid phases in contact with the solution are being dealt with; whilst, in the case of a racemic substance, to which a small proportion of one active isomeride has been added, there is the question only of one solid phase (a racemic one), and this is in contact with a solution saturated with respect to it and partially saturated with respect to the active component. A liquid mixture of d- and l-isomerides, whether they form a racemic liquid or not, only constitutes one phase in the system, and never two, as in the case of a crystalline non-racemic mixture. The error into which Ladenburg has fallen is the more surprising, since Bakhuis Roozeboom has recently contributed a very clear discussion of the subject from the standpoint of the theory of equilibrium (Ber., 1899, 32, 537; Zeit. physikal. Chem., 1899, 28, 494).

We have shown, then, by the foregoing argument, that Ladenburg's method of dealing with liquid externally compensated substances is in disagreement with the very principles from which its author professes to deduce it, namely, the principles of equilibrium. Since, however, the examination of optically active and externally compensated substances in as many directions as possible is urgently desirable at the present time, in order to make certain that the laws of equilibrium have been properly applied, we have made a fresh investigation of some substances of this kind, with results which are quite in accordance with our theoretical argument.

Pseudoracemic and Dextro-Camphorsulphonic Chlorides.

We have previously shown that the sulphonic chloride obtained from the product of the sulphonation of d-camphor with anhydrosulphuric acid, consists of a mixture of the d- and l-isomerides, the former being present in the larger proportion. For many reasons, discussed in earlier papers (Trans., 1893, 63, 548; 1895, 67, 354; 1897, 71, 989), we have also concluded that the externally compensated substance is not truly racemic, but that the antipodes crystallise together, forming a pseudoracemic substance.

We defined a pseudoracemic substance as one in which the enantiomorphously related components are twinned together, and we may therefore take this opportunity of pointing out that the term seems to be understood in a different sense by Roozeboom (Zeit. physikal. Chem., 1899, 28, 494), who attributes to pseudoracemic substances the properties of isomorphous mixtures or solid solutions. As we alone, so far, have worked with pseudoracemic substances, and have observed no marked analogy between isomorphism and pseudoracemism, we cannot share Roozeboom's views as to the nature of such substances; possibly, however, the pinonic acids, recently examined by Fock (Zeit. Kryst. Min., 1899, 31, 479), afford a case of pseudoracemism in the sense in which Roozeboom understands it.

However, according to our views of pseudoracemism, a substance such as crystalline externally compensated camphorsulphonic chloride should behave towards solvents in a manner geometrically similar to that of a non-racemic mixture of optical antipodes, and consequently, on extracting with a solvent a sample of this substance containing a small proportion of one or other isomeride, an optically inactive solution should be obtained; this we find to be the case.

A considerable quantity of crude camphorsulphonic chloride was purified by recrystallisation from ethylic acetate, and a sample was ultimately obtained having the specific rotatory power $[\alpha]_D + 12^\circ$ in chloroform solution; since d-camphorsulphonic chloride has the specific rotatory power $[\alpha]_D + 128^\circ$, the sample contained about 45 per cent. of l- and about 55 per cent. of the d-sulphonic chloride.

Portions of 5 grams of this mixture, when agitated for 5—7 hours at constant temperature with 30 c.c. of various mixtures of light petroleum (b. p. 40—60°) and chloroform, yielded solutions devoid of optical activity when examined in 200 mm. tubes in a polarimeter reading to 0.01°. Our previous conclusion is thus confirmed; crystalline externally compensated camphorsulphonic chloride is not a racemic substance, but is pseudoracemic in the sense of our definition.

But, since externally compensated camphorsulphonic chloride is not racemic in the solid state, there is no reason for expecting that it would be racemic in the pure liquid state at the same temperature, and the probability that it would exist as a racemic substance in dilute solution is even more remote, because, so far as they have been investigated, compounds proved to be racemic in a crystalline condition are known to be wholly resolved into their components in solution.

In order, however, to study the behaviour of mixtures of d- and l-camphorsulphonic chloride in a dissolved condition, the following experiments were made: portions of 3 grams of the same sample as before were completely dissolved in mixtures of chloroform (10 c.c.) and light petroleum (20 c.c.); a mixture of alcohol (30 c.c.) and water (7 c.c.) was then added to the solution, and the whole shaken during 3—4 hours at the ordinary temperature. The liquid, which at the end, as at the commencement of the experiment, was free from crystals, separated when left at rest into two layers; the lower one (about 32 c.c.), we may call the alcoholic, the upper one, the petroleum, solution of camphorsulphonic chloride. Both these solutions were found to be optically active when examined in a 200 mm. tube, the alcoholic solution showing a rotatory power of about $a_D + 0.6^\circ$, the petroleum about $a_D + 0.9^\circ$. A repetition of these experiments with 2 grams of the same sample of sulphonic chloride afforded similar results.

Now, if Ladenburg's application of the method referred to above to liquids were valid, we should have to conclude that dissolved, externally compensated camphorsulphonic chloride is a racemic substance—a conclusion which, as indicated above, is scarcely within the bounds of possibility; there are, moreover, other arguments which lead equally to the conclusion that the sulphonic chloride in the state of solution does not show the behaviour of a racemic compound, so far as the disputed method is concerned. In the first place, the result of shaking together the two solutions of unequal quantities of the two optically active sulphonic chlorides is quite different from that obtained on shaking a solid mixture of a racemic substance and one of its optically active components with a solvent; in the former case, both solutions (the extract and the extracted) remain optically active, whereas in the latter the optical activity is wholly confined to the liquid extract; even granting the existence of a racemic sulphonic chloride in solution, it seems to us that, according to Ladenburg's views, one of the solutions should become optically inactive. In the second place, or rather, putting this same argument differently-if pseudoracemic camphorsulphonic chloride become racemic when it is dissolved in a mixture of chloroform and petroleum, it could not possibly yield an optically inactive solution when a mixture of unequal quantities

of the two antipodes is shaken with such a solvent, whereas our experiments have led to this result.

We have therefore no hesitation in concluding that the experimental evidence which we have brought forward suffices to bear out the truth of the arguments which we have advanced, and that Ladenburg's application to liquids (or wholly dissolved solids) of the principle used in the case of solids is theoretically unsound and incapable of yielding practical results of the slightest value.

One statement by Ladenburg, and one only, seems to be at variance with these conclusions, namely, that a mixture of unequal quantities of d- and l-limonene yields an optically inactive extract when shaken with dilute alcohol insufficient to dissolve the whole. So far as we can judge from the very brief description of the experiment given in his paper (loc. cit.), it seems more probable that the alcoholic solution contained so much water that it dissolved too small a quantity of the mixed limonenes to afford observable optical activity.

Whatever the explanation of this particular experiment, it seemed probable on à priori grounds that the results obtained on extracting an externally compensated liquid, containing a small proportion of one of the antipodes, should be subject to the ordinary law of distribution, just as in the case of optically inactive compounds. This view might perhaps have been put to the test of experiment with the aid of the sample of camphorsulphonic chloride employed above, but this substance does not seem a very suitable one for such a purpose; partly because it gradually hydrolyses in dilute alcoholic solution (but, as we satisfied ourselves, far too slowly to appreciably affect the qualitative results already described), partly because of the necessity for employing four different volatile liquids. For these reasons, we used the enantiomorphously related pinenes for a series of quantitative experiments on the distribution of the components between two liquids.

Dextro- and Lavo-pinens.

The pinenes which we employed were obtained from dextrorotatory American turpentine and levorotatory French turpentine respectively; both were repeatedly distilled in a current of steam with addition of a little sodium carbonate and finally fractionated twice under atmospheric pressure, the fractions boiling at $161-162^{\circ}$ being taken as pinene. Repeated distillation with steam is necessary because, after mixing the two pinenes so as to obtain an optically inactive liquid and then extracting with methylic alcohol, the alcoholic extract becomes optically active unless the purification has been carefully

carried out; in such cases, the activity is doubtless due to the presence of some oxidation product, such as sobrerol.

The rotatory powers of the d- and l-pinene thus obtained having been determined, the hydrocarbons were mixed in such proportion as to give a liquid which appeared optically inactive when examined in a 200 mm. tube. Quantities of 25 c.c. of this inactive oil were then mixed with different small proportions of l-pinene in stoppered bottles and about 25 c.c. of 75 per cent. ethylic alcohol added to each; the sample of l-pinene used had the rotatory power $a_D - 63.33^\circ$ in a 200 mm, tube at 21°.

The bottles were then agitated during four hours at the constant temperature of 22°, by which time it was judged that equilibrium would have been attained; the liquids were then poured into separating funnels, and as soon as the separation into two layers was complete, samples of each layer were run into 200 mm. tubes and examined polarimetrically. The results are given in the following table:

No.	a_{D} of oil, x .	an of solution,	$\frac{x}{y}$.
1 2	0 - 2·64°	0 - 0·19°	13.9
2 8	- 5 ·5 8	-0.84	16.3
4	-7·11	-0.46	15 ·5
5	- 8 ·25	-0.49	16·8
6	- 11·03	-0.75	14.8
7	- 13·75	- 0.98	14.0
8	- 58.78	-2.66	22.1

Pinene and 75 per cent. ethylic alcohol.

It will be seen that in every case both the alcoholic solution and the mixture of pinenes in equilibrium with it are optically active; further, the ratio of the optical activity of the two liquids is approximately constant.

Since the pinenes are miscible in all proportions with absolute ethylic alcohol and dilution with water is necessary in order to make the miscibility imperfect, it seemed desirable to make another series of determinations with a solvent which is not completely miscible with the pinenes. For this purpose we employed methylic alcohol, in which the oil is only moderately soluble, and carried out the experiments just as before, the methylic alcohol and pinene being shaken together during about 5 hours at 20° . The values of $a_{\rm D}$ in 200 mm. tubes for the oils and the alcoholic solutions are given in the following table:

No.	α _D of oil, x.	α _D of solution, y.	$\frac{x}{y}$.
1	0	0	
2 8	– 0 ·90° – 1 ·81	-0.16° -0.88	5·62 5·48
8	- 1·81 - 3·29	-0.68	5· 4 8
4 5 6 7 8 9	- 4·28	- 0.78	5.42
6	- 4·91	-0.82	5.99
7	-6.17	- 1.07	5.77
8	- 6.62	-1.18	5.61
9	- 9·4 6	-1.78	5.47
10	- 10:49	-1.92	5.46

Pinene and methylic alcohol.

The same kind of result is obtained in this as in the previous series of experiments, and strong evidence is thus obtained that the ratio of the observed rotatory powers of the oil and of the alcoholic solution in contact with it is constant. This result proves on analysis to be of considerable interest.

Let us assume in the first place that externally compensated pinene is not racemic. Then in any two determinations with the same solvent, the oils contain, in unit volume, quantities which we may call xl_1 and xl_2 of l-pinene and quantities xl_1 and xl_2 of d-pinene; similarly, unit volumes of the alcoholic solutions in equilibrium with them contain the quantities yl_1 and yl_2 of l-pinene and yd_1 and yd_2 of the d-isomeride. Then, according to the distribution law, the equalities

$$\frac{xd_1}{yd_1} = \frac{xd_2}{yd_2} \quad \text{and} \quad \frac{xl_1}{yl_1} = \frac{xl_2}{yl_2}$$

should hold, provided that the molecular weight of the pinene is the same in the two solvents.

Further, since d- and l-pinene are enantiomorphously related and the differences between the quantities of each present are small compared with the actual quantities, we should expect that

$$\frac{xd_1}{yd_1} = \frac{xd_2}{yd_2} = \frac{xl_1}{yl_1} = \frac{xl_2}{yl_2}$$

whence

2

$$\frac{xl_1 - xd_1}{yl_1 - yd_1} = \frac{xl_2 - xd_2}{yl_2 - yd_2} = \text{const.}$$

But the differences between the quantities of d- and l-pinene present in unit volume are directly proportional to the algebraic sum of the rotations due to the two active components, the length of the polarimeter tube remaining constant. Hence the values of x/y in the

above table should be constant, as they are actually found to be within the limits of experimental error.

It should be pointed out that, since the concentrations xd and xl in the oil are very high, the ratios xd/yd and xl/yl would not be expected to maintain their constancy independent of the total concentration; nevertheless, since the quantities of dextro- and law-o-pinene used in any experiment differ by at most 15 per cent. and the unknown causes affecting the ratios xd/yd and xl/yl are therefore operative to about the same extent on each, the difference of the two ratios $xl_1 - xd_1 = xl_1 - xd_1 = x$

Again, if we assume that externally compensated pinene is racemic in both of the liquid phases, the same result is arrived at. For, replace the quantities d throughout the mathematical statement given above by the quantities r representing racemic material; the compositions of the oils in any two experiments are then xr_1 , xl_1 , and xr_2 and xl_2 , whilst the compositions of the solutes in the corresponding alcoholic solutions are yr_1 , yl_1 , and yr_2 and yl_2 , and from the distribution law

$$\frac{xr_1}{yr_1} = \frac{xr_2}{yr_2} \quad \text{and} \quad \frac{xl_1}{yl_1} = \frac{xl_2}{yl_2}$$

Since the components of the first equality are inactive, the latter does not affect the rotations, and the ratios x/y in the table are proportional to the x/y divided by the y/z, &c.

A third case may of course be imagined, namely, that the externally compensated pinene is racemic in one solution and not in the other; we should then have the equalities involving roots of the component terms and the ratio x/y would not be independent of the total concentration. This eventuality, however, is excluded by the results of the experiments.

We have thus shown that the behaviour of mixtures of unequal quantities of the enantiomorphously related pinenes towards solvents is quite in accordance with the ordinary distribution law and indicates that an optically active pinene exists in the same state of molecular aggregation when dissolved in its optical isomeride as solvent as when dissolved with this isomeride in methylic alcohol; the results of these experiments as they stand are quite independent of any assumption as to the racemic or non-racemic nature of the externally compensated hydrocarbon. Obviously then, these results, in conjunction with those obtained with the camphorsulphonic chlorides, show the futility of attempting to decide between a racemic and a non-racemic liquid by the method employed for this purpose by Ladenburg.

We would point out in conclusion that our use of the term racemic

as applied to liquids must not be construed as an admission of the existence of such compounds; the only evidence favouring the recognition of racemic liquids is Ladenburg's statement that a change of temperature occurs on mixing dextro- and lævo-coniine.

We tender our thanks to the Government Grant Committee of the Royal Society for funds defraying the expenses incurred in this investigation.

University College, Nottingham. GOLDSMITHS' INSTITUTE, NEW CROSS.

CXIV.—Asymmetric Optically Active Nitrogen Compounds. Dextro- and Lavo-a-benzylphenylallyl-methylammonium Iodides and Bromides.

By WILLIAM JACKSON POPE AND STANLEY JOHN PRACHEY.

The only direct evidence pointing to the existence of asymmetric optically active nitrogen compounds is Le Bel's observation (Compt. rend., 1891, 112, 724) that on cultivating Penicillium glaucum in solutions of isobutylpropylethylmethylammonium chloride the liquid acquires a rotatory power of -0° 25' or -0° 30' under favourable conditions. The value of this important observation is, however, considerably lessened by the fugitive nature of the optical activity and by the failure of Marckwald and von Droste-Huelshoff (Ber., 1899, 32, 560) to confirm Le Bel's results.*

Many futile attempts have been made to directly resolve quaternary bases of the type $N(OH)X_1X_2X_3X_4$ into optically active antipodes by means of optically active acids. Thus, Marckwald and von Droste-Huelshoff (*loc. cit.*) attempted to resolve Le Bel's base by the aid of tartaric, camphoric, and mandelic acids whilst Wedekind (*Ber.*, 1899, 32, 517) endeavoured to resolve α -benzylphenylallylmethylammonium hydroxide by means of tartaric and camphoric acids; in no case, however, was an optically active base obtained.

A consideration of the facts led us to the opinion that the failure of these and other attempts had its origin in the facility with which tetralkylammonium salts are decomposed by water and converted into tertiary base and alcohol; we therefore prepared α -benzyl-phenylallylmethylammonium iodide by Wedekind's method (*loc. cit.*) and were successful in resolving it into isomeric optically active bases

Le Bel has recently replied to Marckwald and von Droste-Huelshoff's criticism (Compt. rend., 1899, 129, 548), and has confirmed his previous results.

by using hydroxyl-free solvents containing only small quantities of water. A number of methods, differing in detail, were applied, but we ultimately adopted the following process as affording the best results.

Carefully purified a-benzylphenylallylmethylammonium iodide was mixed with a molecular proportion of the anhydrous silver salt of Reychler's dextrocamphorsulphonic acid and boiled for an hour or so on the water-bath with a mixture of about equal parts of acetone and ethylic acetate, a few drops of water being added when necessary. After separating silver iodide from the gummy solution by filtration, the solvent was distilled off and, on cooling, the residue solidified to a crystalline mass consisting of a mixture of dextro- and lævo-benzylphenylallylmethylammonium dextrocamphorsulphonate.

 $\begin{array}{c} \textit{Dextro-a-benzylphenylallylmethylammonium Dextrocamphorsulphonate,} \\ \textbf{C}_{6}\textbf{H}_{5} \cdot \textbf{CH}_{2} \cdot \textbf{N}(\textbf{C}_{6}\textbf{H}_{5})(\textbf{C}_{3}\textbf{H}_{5})(\textbf{CH}_{3}) \cdot \textbf{SO}_{3} \cdot \textbf{C}_{10}\textbf{H}_{15}\textbf{O}. \end{array}$

By fractionally crystallising the mixture of dextrocamphorsulphonates from boiling acetone, the less soluble constituent, dextro-a-benzylphenylallylmethylammonium dextrocamphorsulphonate was readily obtained in colourless, diamond-shaped plates melting at 169—170°. After drying at 100°, the salt gave the following results on analysis:

0.2005 gave 0.5058 CO₂ and 0.1364 H₂O. C = 68.84; H = 7.56. $C_{27}H_{35}O_4NS$ requires C = 69.08; H = 7.46.

It is very soluble in alcohol or water, less so in acetone, and sparingly soluble in ethylic acetate. The thin, rhomboidal plates deposited from acetone show extinction bisecting the angles; the bisectrix of a large optic axial angle emerges perpendicularly through the large face of the rhomb. The double refraction is positive in sign and the optic axial angle for blue is greater than that for red light.

The rotatory power of the salt was determined in aqueous solution; 0.5256 gram in 25 c.c. gave $a_D + 1.87^\circ$ in a 200 mm. tube, whence $[a]_D + 44.4^\circ$ and $[M]_D + 208^\circ$. As we have previously shown (this vol., p. 1086) that the molecular rotatory power of salts of dextrocamphorsulphonic acid with inactive bases is $[M]_D + 51.7^\circ$, it follows that the basic radicle in the salt now described has the molecular rotatory power of about $+150^\circ$ in aqueous solution.

Lovo-a-benzylphenylallylmethylammonium Dextrocamphoreulphonate.

This salt is contained in the acetone mother liquors, and may be obtained as a granular, crystalline powder by distilling off the solvent and crystallising the residue from boiling ethylic acetate containing a

little acetone; after drying at 100°, it gave the following analytical results:

```
0.1874 gave 0.4710 CO<sub>2</sub> and 0.1284 H<sub>2</sub>O. C = 68.55; H = 7.62. 0.1596 ,, 0.4016 CO<sub>2</sub> ,, 0.1099 H<sub>2</sub>O. C = 68.63; H = 7.64. C<sub>27</sub>H<sub>35</sub>O<sub>4</sub>NS requires C = 69.08; H = 7.46 per cent.
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An aqueous solution of 0.4295 gram in 25 c.c. gave $a_D - 0.64^\circ$ in a 200 mm. tube, whence $[a]_D - 18.6^\circ$ and $[M]_D - 87^\circ$. These numbers show that the substance still contained some of the salt of the dextrobase, because, when pure, its molecular rotatory power would be about $[M]_D - 100^\circ$.

Dextro-a-benzylphenylallylmethylammonium Iodide, $C_6H_5 \cdot CH_2 \cdot N(C_6H_5)(C_8H_5)(CH_8)I$.

On adding to an aqueous solution of dextro-a-benzylphenylallyl-methylammonium dextrocamphorsulphonate the equivalent quantity of potassium iodide dissolved in water, a white, crystalline precipitate immediately begins to separate. After remaining for half an hour, this is collected, well washed with cold water, and purified by crystallising it several times from boiling 50 per cent. alcohol; it melts at 145—147°. The following analytical results were obtained:

```
0.1896 gave 0.3864 CO<sub>2</sub> and 0.0962 H<sub>2</sub>O. C=55.57; H=5.63. 0.1460 ,, 0.2984 CO<sub>2</sub> ,, 0.0732 H<sub>2</sub>O. C=55.74; H=5.57. 0.2561 ,, 0.7640 AgI. I=34.61. C_{17}H_{20}NI requires C=55.89; H=5.48; I=34.79 per cent.
```

A solution of 0.1445 gram, made up to 15 c.c. with a mixture of equal parts of acetone and methylic alcohol, gave $a_D + 1.01^\circ$ in a 200 mm. tube, whence $[a]_D + 52.5^\circ$ and $[M]_D + 192^\circ$.

This salt is much less soluble in hot ethylic alcohol than the externally compensated salt prepared by Wedekind. A hot alcoholic solution of a mixture of the dextro- and inactive iodides, when poured into a 200 mm. tube, gave $a_D + 0.25^\circ$ whilst still warm; on standing, however, crystals were deposited and the solution became inactive, all the dextrorotatory iodide having been deposited. These observations prove that Wedekind's externally compensated iodide is not a racemic compound but merely an ordinary or pseudoracemic mixture of the two antipodes. Corroborative evidence of this is obtained on examining the small crystals of the dextro-iodide deposited from a cooling alcoholic solution; these belong to the orthorhombic system, showing two forms of the kind $\{110\}$ and $\{101\}$. The microcrystallographic characters of the material are identical with those of the inactive iodide and agree with the data given for the latter by Fock (Ber.,

1899, 32, 520); it follows that Fock actually measured crystals of the optically active iodides.

Dextro-a-benzylphenylallylmethylammonium Bromide, $C_6H_5 \cdot CH_2 \cdot N(C_6H_5)(C_2H_5)(CH_2)Br.$

On adding to an aqueous solution of dextro-a-benzylphenylallylmethylammonium dextrocamphorsulphonate the equivalent proportion of potassium bromide dissolved in water, a precipitate of dextro-a-benzylphenylallylmethylammonium bromide was slowly formed; after several recrystallisations from boiling alcohol, it melted at 147—149° and gave the following analytical results:

```
0·1027 gave 0·2409 CO<sub>2</sub> and 0·0586 H<sub>2</sub>O. C=63·97; H=6·34. 0·1164 ,, 0·2731 CO<sub>2</sub> ,, 0·0676 H<sub>2</sub>O. C=64·00; H=6·45. 0·3205 ,, 0·1923 AgBr. Br=25·53. C<sub>17</sub>H<sub>20</sub>NBr requires C=64·15; H=6·29; Br=25·14 per cent.
```

An ethylic alcoholic solution containing 0.1454 gram in 15 c.c. gave $a_D + 1.33^{\circ}$ in a 200 mm. tube, whence $[a]_D + 68.6$ and $[M]_D + 218^{\circ}$.

Lavo-a-benzylphenylallylmethylammonium Iodide.

On mixing the somewhat impure levo-a-benzylphenylallylmethylammonium dextrocamphorsulphonate with potassium iodide as described above, a precipitate of the iodide is obtained from which levo-a-benzylphenylallylmethylammonium iodide may be isolated by repeatedly crystallising the salt from boiling 50 per cent. alcohol, the active substance being less soluble than the inactive mixture. Its ordinary properties are identical with those of its dextro-isomeride; it gave the following analytical results:

A solution of 0.3105 gram, made up to 15 c.c. with a mixture of equal parts of acetone and methylic alcohol, gave $a_D - 2.13^{\circ}$ in a 200 mm. tube, whence $[a]_D - 51.4^{\circ}$.

Lavo-a-benzylphenylallylmethylammonium Bromide.

This substance, prepared from its dextrocamphorsulphonate and purified by crystallisation from boiling alcohol, has properties antipodal to those of its dextro-isomeride. It gave the following results on analysis:

0.1150 gave 0.2695 CO₂ and 0.0660 H₂O. C = 63.92; H = 6.38.

0.1096 , 0.2566 CO_2 , 0.0632 H_2O . C = 63.85; H = 6.41.

0.3447 , 0.2017 AgBr. Br = 24.90.

 $C_{17}H_{20}NBr$ requires C = 64.15; H = 6.29; Br = 25.14 per cent.

A solution of 0.2240 gram, made up to 15 c.c. with absolute alcohol, gave $a_D = 2.01^{\circ}$ in a 200 mm. tube, whence $[\alpha]_D = 67.3^{\circ}$.

We have also succeeded in resolving the inactive iodide into its active components by digesting it with the silver salt of dextro-a-bromocamphorsulphonic acid in acetone solution.

The values of the melting points and rotatory powers given in this preliminary note are only provisional, and we shall subsequently determine them with greater accuracy, using more carefully purified materials.

In the present paper, it is proved that quaternary ammonium derivatives in which the five substituting groups are different, contain an asymmetric nitrogen atom, which gives rise to antipodal relationships of the same kind as those correlated with an asymmetric carbon atom. The method which has enabled us to deal with quaternary bases is now being applied to various other types of substituted ammonium derivatives in order to ascertain the stereochemical nature of pentad nitrogen. We hope shortly to be in a position to publish results obtained with sulphonium derivatives of the type $\mathrm{SX}_1\mathrm{X}_2\mathrm{X}_3\mathrm{I}$.

Our thanks are due to the Government Grant Committee of the Royal Society and to the Research Fund Committee of the Chemical Society for grants enabling us to purchase apparatus and materials used in this work.

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CXV.—Tetrazoline.

By Siegfried Ruhemann and H. E. Stapleton, Scholar of St. John's College, Oxford.

SEVERAL years ago, it was shown by one of the authors (Trans., 1889, 55, 242; 1890, 57, 50; see also Ruhemann and Elliot, Trans., 1888, 53, 850) that by the action of chloroform and alcoholic potash on phenylhydrazine a compound of the formula,

$$C_6H_5\cdot N \stackrel{N:CH}{<_{CH:N}} > N \cdot C_6H_5$$

resulted, which he called diphenyltetrazine. Analogous substances have been produced from ortho- and para-tolylhydrazine. tetrazines for this class of compounds has had to be altered to dihydrotetrazines, since Pinner (Ber., 1894, 27, 987) obtained some members of a similar type with two hydrogen atoms less in the mole-Besides these bases, the formyl derivatives of the hydrazines are also formed in the above reaction, and this fact led to the view that the latter are the first products, which in the second phase of the reaction lose water and condense to the cyclic compounds. Indeed, as shown by Pellizzari (Gazzetta, 1896, 26, ii, 430) and Bamberger (Ber., 1897, 30, 1263), formylphenylhydrazine, on heating, is transformed into dihydrodiphenyltetrazine, for which Pellizzari proposed the suitable name diphenyltetrazoline. The yield, however, according to these authors, is unsatisfactory, as is also the case when the base is prepared by the action of chloroform and alcoholic potash on phenylhydrazine. Lately, Pellizzari (Atti R. Accad. Lincei, [v], 1899, 8, 327, has found that dimethyltetrazoline and monacetyldimethyltetrazoline are formed on heating mono- and di-acetylhydrazine respectively, and that diformylhydrazine yields a non-crystallisable product, which, on treatment with hydrochloric acid, is transformed into tetrazoline hydrochloride.

Our attempts to prepare tetrazoline by digesting hydrazine hydrate with chloroform and alcoholic potash have been unsuccessful, since hydrazine seems hardly to be acted on by these substances. We find, however, that it can readily be obtained by heating monoformylhydrazine. prepared by Schöfer and Schwan's method (J. pr. Chem., [ii], 1895, 51, 180) from hydrazine hydrate and ethylic formate. When monoformylhydrazine is heated for 3 hours in an oil-bath, the temperature of which is gradually raised from 150° to 210°, it loses water, and the residue, when cold, solidifies to a mass of crystals. These are fairly soluble in alcohol, but only sparingly so in chloroform or light petroleum. On dissolving the substance in a boiling mixture of chloroform and absolute alcohol and cooling the solution by ice-water, it separates in exceedingly deliquescent, colourless needles which melt at 82-83°. The yield is very satisfactory. The following analytical data were obtained:

0.2003 gave 0.2085 CO_2 and 0.0980 H_2O . C = 28.37; H = 5.43. 0.1052 ,, 61.8 c.c. moist nitrogen at 24° and 766 mm. N = 66.37. $C_2H_4N_4$ requires C = 28.57; H = 4.76; N = 66.66 per cent.

The aqueous solution of tetrazoline is not alkaline towards litmus; it

gives, with copper sulphate, a blue, and with ferric chloride a red coloration.

Tetrazoline is very soluble in hydrochloric acid, and the hydrochloride, obtained by evaporation of the solution, crystallises from boiling absolute alcohol in long, transparent leaflets which melt at 151—152° (at 150°, according to Pellizzari) and are very soluble in water. On analysis, the hydrochloride gave the following numbers:

0.1112 gave 46 c.c. moist nitrogen at 26° and 767 mm. N = 46.30 0.3065 , 0.3618 AgCl. Cl = 29.20.

 $C_2H_4N_4$, HCl requires N = 46.47; Cl = 29.46 per cent.

The *picrate*, $C_2H_4N_4$, $C_6H_2(NO_2)_8OH$, is precipitated on mixing alcoholic solutions of the base and picric acid. It dissolves only sparingly in alcohol, and crystallises in yellow needles, which melt and decompose at 194—195°.

0.1550 gave 42.5 c.c. moist nitrogen at 22° and 767 mm. N = 31.33. $C_8H_7O_7N_7$ requires N = 31.50 per cent.

Tetrazoline forms, with platinic chloride, a yellow, crystalline compound which has the composition $(C_2H_4N_4)_2$, PtCl₄.

0.2680 gave 0.0945 CO_2 and 0.0445 H_2O . C = 9.61; H = 1.84.

0.1642 ,, 31 c.c. moist nitrogen at 17° and 764 mm. N=22.03.

0.2504 ,, 0.0960 Pt. Pt = 38.34. 0.2326 gave 0.0892 Pt. Pt = 38.35.

 $C_4H_8N_8$, PtCl₄ requires C = 9.51; H = 1.58; N = 22.20; Pt = 38.53 per cent.

Mercuric chloride, even in a dilute aqueous solution of tetrazoline, produces a turbidity which may disappear if the quantity of chloride is small, but is permanent if a sufficient excess is used. The compound, which separates in bunches of colourless needles, is sparingly soluble in water, but dissolves readily in hydrochloric acid, and has the formula $2C_2H_4N_4,3HgCl_2$.

0.4127 gave 0.2930 HgI. Hg = 61.20.

0.3550 ,, 0.2520 HgS. Hg = 61.19. $C_4H_8N_{81}3HgCl_2$ requires Hg = 61.16 per cent.

The aqueous solution of tetrazoline gives a yellowish, crystalline precipitate with auric chloride, and with silver nitrate yields colourless needles of a silver compound which explodes on heating. We are engaged in the further study of tetrazoline, and shall shortly lay the results be ore the Society.

GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

CXVI.—Action of Hydrolytic Agents on a-Dibromocamphor. Constitution of Bromocamphorenic Acid.

By ARTHUR LAPWORTH.

When β -dibromocamphor is warmed with strong aqueous alkalis, it dissolves, and acid products are obtained; these do not appear to have been examined, but their formation indicates that hydrolysis of the dibromocamphor has occurred, and it is probable that they include derivatives of a-campholenic acid. This acid has been isolated from the product of the action of moist sodium amalgam on β -dibromocamphor (Kachler and Spitzer, *Monatsh.*, 1882, 3, 216; 1883, 4, 643), and its presence is doubtless due to the occurrence of combined reduction and hydrolysis.

The formation of α -campholenic acid by two different reactions, from β -dibromocamphor on the one hand, and from camphoroxime on the other, would certainly seem to indicate that the substance is related to camphor in a simple manner. In the present paper, however, evidence is brought forward which shows that obscure changes in structure may occur under conditions which cannot be regarded as violent, and it is of especial interest that a change of this kind occurs in a reaction almost exactly analogous to that whereby β -dibromocamphor affords α -campholenic acid.

Action of Silver Compounds on a-Dibromocamphor.

 α -Dibromocamphor, unlike the β -derivative, when treated with alkalis, or with sodium amalgam, is merely reduced, and hitherto no hydrolytic effect appears to have been observed. It was in the hope of producing such an effect that the following experiment was made. A solution of α -dibromocamphor in alcohol was warmed on the waterbath in a reflux apparatus, and to the hot solution small quantities of finely powdered silver nitrate were added. After each addition cloudiness ensued, and was followed by a copious deposition of silver bromide, the addition of silver salt being interrupted when this cloudiness was no longer produced. The whole was heated for about an hour, and after the addition of hydrochloric acid, in amount sufficient to precipitate the excess of silver, the liquid was filtered, evaporated at a low temperature, and then distilled in steam; a solid product, smelling strongly of camphor, passed over, le ving an oily residue.

The solid product in the distillate was collected an! carefully fractionated, when it resolved itself for the most part into camphor and monobromocamphor. The less volatile portion, on examination,

was found to contain monobromocamphor and unaltered dibromocamphor.

The oily residue in the distilling flask could be separated into two portions by means of sodium carbonate solution; the portion insoluble in sodium carbonate was for the most part unaltered dibromocamphor, but contained a small quantity of nitrogenous substance soluble in hot caustic potash. The portion dissolved by sodium carbonate separated on the addition of an acid as a brown, apparently amorphous precipitate, and after purification by dissolving in sodium carbonate and reprecipitating with acid, was crystallised from alcohol.

This acidic substance separated from alcohol in beautiful, white needles, and from ethylic acetate in large, transparent, monoclinic plates; it melted at 159°. It dissolved slowly in cold dilute sodium carbonate with effervescence, and the solution at once discharged the colour of dilute potassium permanganate. On treatment with bromine, it evolved hydrogen bromide, and yielded a neutral substance which separated from alcohol in needles and melted at 152°. The substance obtained by the action of silver nitrate on α -dibromocamphor had therefore the properties of an unsaturated $\beta\gamma$ - or $\gamma\delta$ -acid. It contained bromine, and gave the following results on analysis:

0.2073 gave 0.3701 CO₂ and 0.1110 H₂O.
$$C = 48.7$$
; $H = 6.0$. $C_{10}H_{15}O_{2}Br$ requires $C = 48.6$; $H = 6.1$ per cent.

It was finally found by direct comparison to be identical in all respects with bromocamphorenic acid, first obtained by Forster from dibromocamphor in an indirect manner (Trans., 1896, 69, 46).

This action of silver nitrate appears at first sight to be merely one of hydrolysis in accordance with the equation

$$C_{10}H_{14}OBr_{2} + H_{2}O = C_{10}H_{15}O_{2}Br + HBr_{3}$$

and therefore more or less analogous to the hydrolysis of β -dibromocamphor by sodium amalgam, and it is now clear that the production of this substance accounts for the formation of homocamphoronic acid when a dibromocamphor is oxidised in presence of silver nitrate (this vol., p. 992).

When, in the above experiment, acetic acid is used instead of alcohol as a solvent, nitrous fumes are rapidly evolved, and the solution on cooling frequently deposits beautiful needles of bromocamphorenic acid. The yield of this compound, although greater than in the former case, did not in any instance greatly exceed 15 per cent. of that theoretically possible.

In order to make certain that the nitric acid or nitrous fumes disengaged during the reaction played no part in the production of bromocamphorenic acid, the experiments were repeated with silver acetate instead of nitrate, but the results only differed as regards the length of time required to complete the reaction, and the proportion of acid produced.

a-Dibromocamphor in alcoholic solution is rapidly attacked by moist silver oxide, and, in addition to the above products, a small quantity of a yellow, oily substance is formed; this is insoluble in alkalis, and, as it gives a crystalline compound on treatment with semicarbazide acetate, is probably a ketone: it is not camphorquinone, however, as it is not volatile in steam.

Action of Mercury and Lead Compounds on a-Dibromocamphor.

Interesting results having been obtained with silver salts, it was thought desirable to examine the action of other metallic compounds on a-dibromocamphor. Mercurous nitrate was first chosen, as it resembles silver nitrate in yielding a very sparingly soluble bromide.

On adding mercurous nitrate to a hot solution of a-dibromocamphor in acetic acid, nitrous fumes were at once evolved, and a precipitate of mercurous bromide was produced. If the action was interrupted after about 15 minutes, it was found that a small quantity of bromocamphorenic acid could be isolated, but the amount formed was considerably smaller than when silver salts were used.

It is interesting that lead salts and moist lead oxide seem to have little or no effect on a-dibromocamphor under conditions similar to the above. In order to induce any marked decomposition with lead oxide, it was necessary to heat the materials with water in sealed tubes at 120-150°, and the experiments showed that when any appreciable action occurred, the organic matter was almost entirely carbonised. In one instance, however, the aqueous solution had acquired a distinct yellow colour, and on distilling the contents of the tube with steam, it was found that the first few drops of the distillate were bright yellow, and deposited a few yellow needles. Although the quantity was too small for analysis, the substance was easily identified, as it melted at 196-198°, approximately the melting point of camphorquinone (Claisen, Ber., 1889, 22, 530). It sublimed with great readiness, its aqueous solution was decolorised by sodium hydrogen sulphite, the colour being restored by means of acid, and, when examined in polarised light, the crystals could not be distinguished from those of camphorquinone prepared by the ordinary method. It may be mentioned that from the same tube a considerable quantity of monobromocamphor was obtained by continuing the steam distillation.

In order to determine whether bromocamphorenic acid was produced in the foregoing reaction, the carbonised contents of four tubes were united and boiled with a solution of sodium carbonate. No

appreciable quantity of bromocamphorenic acid was obtained from the filtrate after acidification, but on extracting the acid liquid with ethylic acetate and evaporating, a small quantity of a crystalline acid was isolated, which, after purification, melted with some effervescence at 184°, but when allowed to solidify, melted again at temperatures varying between 80° and 200°. It yielded an anhydride melting at about 215° on treatment with acetyl chloride, and its whole behaviour suggested that it was camphoric acid. This was confirmed by analysis.

0.1014 gave 0.2216 CO₂ and 0.0760 H₂O. C = 59.6; H = 8.3. $C_{10}H_{16}O_4$ requires C = 60.0; H = 8.0 per cent.

It is possible, of course, that the formation of camphoric acid from dibromocamphor in this way is due to the oxidation of camphor or monobromocamphor produced at an intermediate stage, but it seems more probable that hydrolysis has taken place, with the production of camphorquinone, which would readily yield camphoric acid under the above conditions.

Oxidation of Derivatives of Bromocamphorenic Acid.

In the endeavour to obtain fairly large quantities of homocamphoronic acid by a convenient method, a large number of experiments were made with derivatives of bromocamphorenic acid, and a brief account of the results may be given.

The method used by Forster (loc. cit.), namely, oxidation of bromocamphorenic acid with ice-cold permanganate, was found to give very poor yields of the desired product, and was inconvenient on account of the large quantity of liquid necessarily involved.

Oxidation of bromocamphorenic acid with dilute nitric acid, even in presence of silver nitrate, also gave poor results, as it was almost impossible to avoid the formation of a stable nitro-derivative, and the substance itself is so sparingly soluble in the nitric acid that the action is excessively slow. In every case, however, some small quantity of homocamphoronic acid was obtained. Chromic acid was found to be quite useless as an oxidising agent.

Dibromocampholid was next tried, and was oxidised in various ways. With dilute nitric acid and silver nitrate, fairly good results were obtained, but the action was slow; on evaporating the filtrate after several days treatment with the oxidising mixture, homocamphoronic acid was at once obtained, apparently uncontaminated with any secondary product. The yield was in each case about 15—20 per cent. of that theoretically possible.

a-Monobromocampholid, the lactone obtained by treating bromo-

camphorenic acid with sulphuric acid (Forster, loc. cit.) was found to be the most suitable substance for the purpose. It is rapidly attacked by a solution of silver nitrate in dilute nitric acid (1 vol. of nitric acid of sp. gr. 1.42, and 1½ vols. of water), and if the mixture is heated on the water-bath for about 60 hours, homocamphoronic acid, sometimes amounting to more than 60 per cent. of the bromocampholid used, may be readily obtained. In this case also, the resulting homocamphoronic acid seems to be practically pure, and only very small quantities of any secondary products are present. A minute quantity of an acid which did not yield an anhydride when heated at 180° was observed, but the amount was less than 1 per cent. of that of the homocamphoronic acid obtained.

Constitution of Bromocamphorenic Acid.

Sufficient is now known of the properties of bromocamphorenic acid and its derivatives to warrant a discussion of the probable structural formula of this substance. It has been shown by Forster that the acid is unsaturated and that it contains one closed chain (loc. cit.). It is practically certain, moreover, that the grouping 'CH:CBr' forms a portion of the closed chain, as the substance, when treated with ice-cold permanganate, rapidly loses bromine, and is subsequently converted into homocamphoronic acid, an open-chain tricarboxylic acid. This view represents the oxidation as resulting in the conversion of an acid COOH·C7H18 COOH and the fact

that bromine is at once eliminated receives explanation in the circumstance that the glycol produced as the first step in the oxidation would contain the radicle >CBr·OH, from which hydrogen bromide would be split off immediately with formation of the >CO group. This also supplies a simple explanation of the fact, among others, that a-monobromocampholid, when hydrolysed, yields an acid having the formula $C_{10}H_{16}O_8$ (Forster, *loc. cit.*).

It was at one time thought possible that homocamphoronic acid might be formed from an intermediate β -ketonic acid by hydrolysis, but a number of important considerations have led to the rejection of this view.

Of the formulæ containing the radicle 'CH:CBr', which can be devised to represent bromocamphorenic acid, in view of its simple relationship to homocamphoronic acid, only two,

correspond in any simple way with any possible formula for α-dibromocamphor. These, moreover, are the only expressions containing in addition the group :CMe·COOH, which is almost certainly present in bromocamphorenic acid for the following reasons.

It is now scarcely open to question that camphoric acid contains the complex $C \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_2 \subset CMe_$

C—CH—CH₂
camphor contains the group : | , in which the transposi:C—CMe·CO

tion of the 'CH₂' and 'CO' groups is not possible (compare Noyes, Ber., 1899, 32, 2289 and 2290). a-Dibromocamphor must therefore

C—CH—CBr₂

contain the group : | (compare Lowry, Trans., 1898, :C—CMe·CO

73, 569, 1001). In its transformation into bromocamphorenic acid, it is at least certain that the 'CO' group is converted into 'COOH, and from what has been said it must be clear that separation of the 'CO' and 'CBr₂' groups has occurred. Although some curious alteration in the structure of the molecule occurs, consisting evidently of the absorption into a ring of the carbon to which the bromine atoms are attached, it is altogether unnecessary to imagine that the change has extended to the group :CMe'CO, which, it is worthy of note, is present in homocamphoronic acid.

We have now to choose between the formulæ I and II, and there can be little doubt which of these is to be preferred. The latter represents a $\gamma\delta$ -unsaturated acid, and in all probability an acid of this formula would be readily converted into the corresponding $\beta\gamma$ - or $\alpha\beta$ -acid, whilst such an occurrence is impossible with an acid represented by formula I. There are, morever, a large number of facts which, taken together, speak in favour of formula I as against formula II. Thus in the expressions for α -monobromocampholid and for camphononic acid derived from formula II, namely:

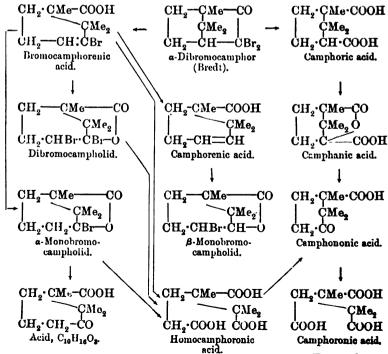
$$\begin{array}{c|cccc} \mathbf{CMe_2} \cdot \mathbf{CMe} & \mathbf{CMe_2} \cdot \mathbf{CMe} \cdot \mathbf{COOH} \\ & \mathbf{CH_2} & \mathbf{CH_2} & & & & & & & & \\ & \mathbf{CH_2} & \mathbf{CBr} & & & & & & & \\ & \mathbf{CH_2} & \mathbf{CO} & & & & & & \\ & \mathbf{CH_2} & \mathbf{CO} & & & & & \\ & \mathbf{CO} & & & & & & \\ \end{array}$$

there is apparently no reason why oxidation should not take place at the points marked (b) as well as at those marked (a), whereas in fact only one product in each case can be isolated.

All these difficulties disappear when formula I is used, and this expression explains in a most satisfactory manner all the facts bearing on the question which have been observed by Forster and by the author.

It is difficult to understand the change which a-dibromocamphor undergoes in its conversion into bromocamphorenic acid, but it does not become easier if any of the other possible formulæ for the latter substance be employed. The enlargement of a ring of carbon atoms by the inclusion of a carbon atom hitherto outside the ring is by no means an unknown phenomenon, and an assumption very similar to the one employed here, has been recently put forward by Wagner and Brickner to explain the conversion of pinene into derivatives of camphene (Ber., 1899, 32, 2323).

It is worthy of remark that the formula above suggested as the most suitable for bromocamphorenic acid bears to Bredt's formula for dibromocamphor a relationship which could not, in the circumstances, be more simple. This relationship, as well as that connecting a number of important compounds the properties of which have necessarily been considered in eliminating the improbable formulæ, is exhibited in the following scheme:



It is hoped that the investigation, which is still being carried on, may elicit further evidence bearing on the question discussed in the paper.

Much of the expense incurred during the work has been defrayed by a grant from the Research Fund of the Chemical Society, and for this help the author desires to express his indebtedness.

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CXVII.—Camphoroxime. Part III. Behaviour of Camphoroxime towards Potassium Hypobromite.

By MARTIN ONSLOW FORSTER, Ph.D., D.Sc.

On the failure of an attempt to prepare a-bromocamphoroxime by the direct action of bromine on camphoroxime dissolved in glacial acetic acid (Trans., 1897, 71, 1030), I was led to study the behaviour of the oxime towards an alkaline solution of potassium hypobromite.

When treated with this agent, camphoroxime undergoes simultaneous bromination and oxidation, a quantitative yield of the compound, $C_{10}H_{16}BrNO_2$, being readily obtained if certain conditions are observed. The change is expressed by the equation

$$C_{10}H_{17}NO + 2KOBr = C_{10}H_{16}BrNO_{2} + KOH + KBr.$$

The new derivative is not an oxime, being indifferent towards benzoic chloride, but it contains a nitroso-group, produced by removal of hydrogen from the oximido-residue. It is remarkably indifferent towards aqueous potash, from which it may be distilled without undergoing apparent change, whilst hot concentrated nitric acid scarcely dissolves it, and, at first, has no perceptible action on it.

On dissolving the bromonitroso-derivative in concentrated sulphuric acid, the elements of water are withdrawn, and the compound $C_{10}H_{14}BrNO$, is produced. Unlike the substance from which it is obtained, this compound does not give Liebermann's reaction for nitroso-derivatives; moreover, cold concentrated nitric acid dissolves it immediately, whilst hot hydrochloric acid transforms it into an isomeride which yields a benzoyl derivative by the Schotten-Baumann method. These isomeric substances are optically inactive, although the initial compound is strongly levorotatory.

Under the influence of hot caustic alkalis, the isomerides, C₁₀H₁₄BrNO, break up in a remarkable manner, yielding a nitrile of the empirical

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formula C₉H₁₈N. The production of such a compound involves elimination of carbon monoxide and hydrogen bromide in accordance with the equation,

$$C_{10}H_{14}BrNO = C_{9}H_{18}N + CO + HBr.$$

The nitrile, when hydrolysed with alcoholic potash, yields the corresponding amide, which has the formula $C_9H_{15}NO$, and is therefore isomeric with the amides of isolauronolic and camphoceenic acids; these, however, melt at $129-130^\circ$ (G. Blanc, Compt. rend., 1896, 123, 749) and 155° (Jagelki, Ber., 1899, 32, 1506) respectively, whereas the new amide melts at 90°. Nevertheless, its relation to isolauronolamide must of necessity be a close one, because hydrochloric acid converts it into that substance along with isolauronolic acid.

It has been shown that when sodium orthoethylic camphorate is submitted to electrolysis, the ethylic salt of campholytic acid is formed (Walker, Trans., 1893, 63, 495); the acid itself is also obtained by the action of nitrous acid on dihydroaminocampholytic acid, produced on eliminating carbon monoxide from β-camphoramic acid, NH₂·CO·C₈H₁₄·COOH, by the agency of sodium hypobromite (Noyes, Ber., 1895, 28, 547). Electrolysis of sodium orthoethylic camphorate also yields isolauronolic acid, first described by Walker, who then called it camphothetic acid (loc. cit.); the production of this compound from sulphocamphylic acid was recorded about a month later by Koenigs and Hoerlin (Ber., 1893, 28, 811), from whom it received its present name.

These isomerides, isolauronolic and campholytic acids, are now regarded as the cis- and cistrans-modifications respectively of a single acid, mainly because both contain an unsaturated linking in the αβ-position, and also on account of the readiness with which isolauronolic (cis-campholytic) acid is produced from the labile isomeride. Mere contact with cold dilute sulphuric acid at ordinary temperatures will suffice to convert the liquid campholytic acid into solid isolauronolic acid (Noyes, Ber., 1895, 28, 548), and in a private communication, Professor Walker informs me that an impure specimen of campholytic acid which has remained in his possession for some years, has now become almost entirely transformed into isolauronolic acid.

Neither the formula $(CH_3)_2C \leftarrow CH_2 - CH_2$. Neither the formula $(CH_3)_2C \leftarrow C(CH_2)$. C·COOH, by which Blanc represents the structure of isolauronolic acid (Bull. Soc. Chim., 1898, [iii], 19, 534; compare also 1899, [iii], 21, 830), nor the expression $(CH_2)_2C \leftarrow CCOOH$, adopted by W. H. Perkin, jun. (Trans., 1898, 73, 796), suggests any reason for supposing that one of the two possible structural isomerides which have the unsaturated linking in the

aβ-position would be more stable than the other. There is consequently every justification for the accepted view of the relation between campholytic and isolauronolic acids, and the readiness with which the new amide is converted into isolauronolamide and isolauronolic acid renders it highly probable that the substance in hand is the hitherto unknown amide of campholytic acid. Up to the present, however, it has not been found possible to verify this anticipation experimentally, because the amide resists the action of alcoholic potash, and the employment of an acid as hydrolytic agent is obviously precluded; it is noteworthy that isolauronolamide is described by Blanc as being very indifferent towards alcoholic potash.

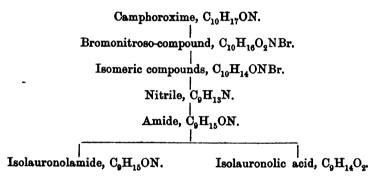
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The passage from camphoroxime to isolauronolic acid is represented in the following scheme:



As regards the constitution of the bromonitroso-compound and the isomerides obtained from it on withdrawing the elements of water, discussion at the present moment would be premature. on the behaviour of menthoneoxime, isonitrosocamphor, thymoquinoneoxime, and carvoxime towards alkaline hypobromite have been carried out for purposes of comparison, but no useful information has been obtained as yet from these sources. It is clear, however, that the initial substance does not belong to the class which includes bromonitrosopropane, obtained by Piloty from acetoxime and bromine in presence of pyridine (Ber., 1898, 31, 452), because it contains more oxygen than camphoroxime, whereas the conversion of acetoxime into bromonitrosopropane merely involves removal of hydrogen and addition There is every probability that the substance is a true bromonitroso-derivative containing the complex > CBr·NO, the presence of the group, >C:NOBr being rendered highly improbable by the stability of the compound towards aqueous alkali. The disposition of the oxygen atom which has been added to the molecule can be ascertained only by further study, and the work is being continued from this point of view.

EXPERIMENTAL.

Action of Potassium Hypobromits on Camphoroxime.

A solution of potassium hypobromite was first prepared by dissolving 600 grams of caustic potash in 1000 c.c. of water, cooling the solution with crushed ice, and adding 400 grams of bromine to the well-stirred liquid. 100 grams of finely-powdered camphoroxime were next converted into a thin paste with 200 c.c. of water, and treated with 200 grams of caustic potash dissolved in 500 c.c. of water. The oxime, suspended and in part dissolved in the alkali, and cooled by fragments of ice, was finally mixed with the cold solution of hypobromite, which quickly transformed it into a pale green solid having a faint, pungent odour. After 24 hours, the product had risen to the surface in a compact mass, and the clear liquid was therefore removed with the aid of a syphon; the green solid was washed several times with water, and finally spread in thin layers on blotting paper.

On exposure to air, the substance became pale yellow, but retained its pungent odour. The yield approached that required by theory. When crystallised twice from hot alcohol, the compound was obtained in snow-white, fern-like aggregates, and melted at 220°, forming a colourless liquid which immediately began to turn red and evolve gas. The substance could not be powdered, because moderate pressure transforms it into tough, camphor-like masses; it was therefore cut into small fragments for analysis and dried at 80°.

0.2708 gave 0.4570 CO_2 and 0.1503 H_2O . C = 46.02; H = 6.16. 0.4048 ,, 19.8 c.c. moist nitrogen at 23° and 769 mm. N = 5.57. 0.2376 ,, 0.1693 AgBr. Br = 30.32. C. H. O. NBr requires $C = 45.80 \cdot H = 6.10 \cdot N = 5.35 \cdot Br = 30.53$

 $C_{10}H_{16}O_2NBr$ requires C=45.80; H=6.10; N=5.35; Br=30.53 per cent.

The new derivative from camphoroxime gives Liebermann's reaction for nitroso-compounds. It distils readily in an atmosphere of steam and is excessively soluble in benzene or petroleum. Concentrated nitric acid has no action on the substance, which merely fuses to a yellow oil when heated with it, and resolidifies on cooling; it is also indifferent towards boiling aqueous potash, from which it may be distilled without undergoing any apparent change.

A solution containing 0.2475 gram dissolved in 25 c.c. of absolute alcohol at 23° gave $a_D = 1^{\circ}5'$ in a 2-dcm. tube, whence $[a]_D = 54.7^{\circ}$. A solution of 0.5061 gram in 25 c.c. of benzene at 21° gave $a_D = 2^{\circ}39.5'$ in the same tube, corresponding to $[a]_D = 65.6^{\circ}$.

A determination of the molecular weight in benzene solution gave the following result:

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Molecular weight of compound, $C_{10}H_{16}O_2NBr = 262$.

Grams of benzene.	Grams of substance.	Grams of substance in 100 grams of solvent.	Depression of freezing point.	Molecular weight deduced.
16:66	0·2812	1·3875	0·292°	282·8
	0·3852	2·0120	0·428	230·3
	0·4372	2·6242	0·539	238·5

Reduction of the Bromonitroso-compound.—5 grams were dissolved in glacial acetic acid and treated with 5 grams of zinc dust while the liquid was cooled with ice. On diluting the filtered solution with water, a pale yellow oil separated, and after several days, colourless crystals were deposited. The oil had the odour of campholenonitrile, which is generally produced when camphoroxime is heated with glacial acetic acid and zinc dust. The solid substance was dissolved in hot petroleum, which deposited the characteristic crystals of camphoroxime, melting at 118° ; a 3.2 per cent. solution in absolute alcohol gave $\lceil \alpha \rceil_{\rm D} -41.1^{\circ}$.

Action of Concentrated Sulphuric Acid on the Bromonitroso-compound.

A beaker containing 800 c.c. of concentrated sulphuric acid was surrounded with a freezing mixture. When the temperature of the acid had fallen below 0°, the bromonitroso-compound was added in small quantities at a time; meanwhile the liquid was well stirred and maintained at a temperature below 10°. An orange coloration was developed on first adding the substance, but the liquid rapidly became dark brown, and a highly scented, viscous oil rose to the surface. When 100 grams of material had been added, the oil was removed, and the acid allowed to flow in a thin stream on to finely crushed ice, which precipitated a pale yellow solid. The latter was collected, washed, spread on porous earthenware, and dissolved in the minimum quantity of boiling alcohol, which was then rapidly cooled. The yield was disappointing, as operations involving 200 grams of the bromonitroso-compound have never furnished more than 75 grams of the crystallised product, and on one occasion only 50 grams were obtained; the theoretical amount, allowing for the production of the fragrant oil, is 170 grams. In order to secure a comparatively good yield, it is absolutely essential to maintain the sulphuric acid in constant agitation while the bromonitroso-compound is being added; the latter rises to the surface of the acid if this remains undisturbed, where it becomes heated, and blackens, evolving gas. Even when

the liquid is efficiently cooled and agitated, alcohol extracts from the crude product a considerable quantity of tarry matter.

The substance formed by dehydration of the bromonitroso-compound is sparingly soluble in cold, but readily in boiling alcohol, from which it crystallises in long, lustrous, transparent needles; it is readily soluble in benzene.

0.2460 gave 0.4382 CO₂ and 0.1322 H₂O. C=48.58; H=5.97. 0.2394 ,, 12.3 c.c. moist nitrogen at 21° and 756 mm. N=5.82. 0.1977 ,, 0.1508 AgBr. Br=32.46.

 $C_{10}H_{14}ONBr$ requires $C=49\cdot18$; $H=5\cdot74$; $N=5\cdot74$; $Br=32\cdot79$ per cent.

It has no definite melting point, but shrinks and darkens at about 210°, becoming completely charred at 220°; it is slightly volatile on the water-bath, and sublimes in minute, transparent needles. The derivative does not give Liebermann's reaction, and is saturated towards bromine in chloroform, but a hot solution in dilute sulphuric acid quickly reduces potassium permanganate. Warm concentrated nitric acid decomposes it, liberating gas, but hot concentrated sulphuric acid and boiling pyridine are without action on it.

As already stated, this compound is destitute of rotatory power. A 4 per cent. solution in benzene and a 1 per cent. solution in alcohol were examined in a 2-dcm. tube and found to be inactive.

Conversion of the Compound, $C_{10}H_{14}ONBr$, into an Isomeride.

The compound, $C_{10}H_{14}ONBr$, was powdered and covered with concentrated hydrochloric acid, which was then boiled during several minutes; on dissolving the product in hot water and allowing the filtrated liquid to cool, colourless needles were deposited. This modification is also obtained by boiling an alcoholic solution of the compound with a few c.c. of concentrated hydrochloric acid, and crystallises from alcohol in large, transparent, six-sided plates; it melts at 240° to a colourless liquid which does not decompose, and is slightly volatile at 100° .

0.2548 gave 0.4596 CO_2 and 0.1347 H_2O . C=49.19; H=5.87.

0.3633 ,, 18·1 c.c. moist nitrogen at 24° and 769 mm. N = 5.65. 0.2358 ,, 0.1820 AgBr. Br = 32.84.

 $C_{10}H_{14}ONBr$ requires $C = 49 \cdot 18$; $H = 5 \cdot 74$; $N = 5 \cdot 74$; $Br = 32 \cdot 79$ per cent.

The substance does not give Liebermann's reaction, and behaves like a saturated compound towards bromine dissolved in chloroform, and also towards a hot solution of potassium permanganate; it under-

goes no change when a solution in glacial acetic acid, or alcoholic hydrochloric acid, is boiled with zinc dust. It resembles the first modification in being optically inactive, but differs from it in its behaviour towards benzoic chloride, with which it yields a benzoyl derivative. This crystallises from alcohol in lustrous scales and melts at 174—176°.

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Behaviour of the Compounds, C₁₀H₁₄ONBr, towards Caustic Soda.

A boiling, aqueous solution of caustic soda eliminates hydrogen bromide and carbon monoxide from the compound, $C_{10}H_{14}ONBr$, and from its isomeride, giving rise to a nitrile of the formula $C_0H_{13}N$.

100 grams of the finely powdered substance were heated with a solution of 40 grams of caustic soda in 300 c.c. of water; the operation was conducted in a reflux apparatus on the water-bath and continued during half an hour. A volatile oil soon appeared in the condenser, and the suspended solid aggregated to a pasty mass beneath the liquid. After the period specified, the condenser was rearranged for distillation, and a current of steam was passed through the alkali until the bromo-compound was completely decomposed. On extracting the distillate with ether, drying the extract with calcium chloride, and evaporating the ethereal solution, 50 grams of the nitrile were obtained; the aqueous residue in the distillation flask was concentrated on the water-bath and yielded 6 grams of the solid amide described below.

The nitrile is a limpid, colourless oil having an agreeable, camphor-like odour, it boils at 198—199° under 760 mm. pressure, and has a sp. gr. 0.9038 at 24°.

0.2213 gave 0.6466 CO_2 and 0.1940 H_2O . C=79.68; H=9.74. 0.1560 , 14.1 c.c. moist nitrogen at 20.5° and 764 mm. N=10.37. $C_9H_{18}N$ requires C=80.00; H=9.63; N=10.37 per cent.

The substance reduces a cold solution of potassium permanganate instantly, and also decolorises bromine dissolved in chloroform. A specimen examined in a 2-dcm. tube was feebly dextrorotatory, giving $a_{\rm D} + 0^{\circ}$ 46', an angle so small, in view of the inactivity of the original compound, as to suggest the presence of some optically active impurity.

In view of the fact that the elements of hydrogen bromide and carbon monoxide are withdrawn from the compound, $C_{10}H_{14}ONBr$, by the action of caustic soda, it became necessary to test the alkaline

residue in the distillation flask for sodium formate. The liquid was accordingly acidified with dilute sulphuric acid, and a current of steam passed through it. Formic acid was recognised without difficulty in the distillate, which had a faint, pungent odour, and was strongly acid towards litmus; silver nitrate gave a precipitate undergoing immediate reduction on heating, and a specimen of the characteristic lead formate was obtained.

Hydrolysis of the Nitrile.

25 grams of the nitrile were heated with a solution of 20 grams of caustic potash in alcohol during 30 hours in a reflux apparatus. Water was then added to the liquid, from which alcohol was removed by evaporation; a yellow oil floated on the surface, and rapidly crystallised as it cooled. The product was collected, drained on porous earthenware, and recrystallised from boiling light petroleum.

0.2117 gave 0.5479 CO_2 and 0.1913 H_2O . C = 70.58; H = 10.04.

0.1812 , 0.4662 CO_2 , 0.1613 H_2O . C = 70.17; H = 9.89.

0.2235 ,, 18.4 c.c. moist nitrogen at 24° and 769 mm. N=9.34. $C_9H_{15}ON$ requires C=70.59; H=9.80; N=9.15 per cent.

The amide is scarcely soluble in cold, but dissolves more freely in boiling petroleum, from which it separates in highly lustrous needles melting at 90°; it dissolves readily in alcohol, and is also soluble in boiling water, crystallising in flat, lustrous needles as the liquid cools.

Behaviour towards Hydrochloric Acid.—The recrystallised amide dissolved freely in cold concentrated hydrochloric acid, but on boiling the solution in a reflux apparatus it rapidly became turbid, owing to the separation of an oil; the latter immediately crystallised on cooling the contents of the flask. On collecting the product with the aid of a filter pump, it was found that crystallisation from boiling water containing a little sodium carbonate yielded a substance having the empirical formula of the original amide.

0.2000 gave 0.5145 CO₂ and 0.1759 H₂O. C = 70.16; H = 9.77. $C_9H_{15}ON$ requires C = 70.59; H = 9.80 per cent.

Moreover, the compound crystallised in highly lustrous needles exactly resembling the substance from which it was obtained. It melted, however, at 129—130°, the melting point of isolauronolamide (G. Blanc, Compt. rend., 1896, 123, 749).

During the conversion of the amide melting at 90° into isolauronolamide, colourless crystals collected in the condenser. These were analysed, with the following result:

0.1714 gave 0.4399 CO₂ and 0.1408 H₂O. C = 70.00; H = 9.12. $C_9H_{14}O_2$ requires C = 70.13; H = 9.09 per cent.

The substance melted at 132—133°; a solution in chloroform was indifferent towards bromine, but when dissolved in sodium carbonate, the acid decolorised potassium permanganate instantly. This is the behaviour of isolauronolic acid, and it was found that the melting point of the preparation obtained in the manner just indicated was not depressed by admixture with a specimen of isolauronolic acid sent to me for the purpose of comparison by Prof. W. H. Perkin.

The action of hydrochloric acid on the amide melting at 90° precludes the use of this agent for the purpose of hydrolysis. Unfortunately, however, alcoholic potash is almost without action on the substance. In one experiment, 10 grams were heated during 50 hours with a concentrated solution of caustic potash in alcohol, and practically the whole amount of the amide was recovered on dilution with water and evaporation. On heating 5 grams with 15 c.c. of a 50 per cent. aqueous solution of potash in a sealed tube at 120° during 6 hours, and removing the unaltered amide, the aqueous liquid yielded on acidification about 0.5 gram of an oily acid; for reasons already stated, it seems probable that this compound is campholytic acid (Walker, Trans., 1893, 63, 495), and further attempts to identify it are being made.

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CXVIII.—Influence of an Unsaturated Linking on the Optical Activity of Certain Derivatives of Bornylamine.

By MARTIN ONSLOW FORSTER, Ph.D., D.Sc.

As a result of investigating certain alkyl derivatives of bornylamine (Forster, this vol., p. 934), it was found that, although the specific rotatory power of the monalkyl derivatives considerably exceeds that of the original base, the optical activity of symmetrical dialkyl derivatives approximates very closely to that of bornylamine itself. Ethylbornylamine, for instance, has the specific rotatory power $[a]_D + 90 \cdot 3^\circ$ in benzene, but dimethylbornylamine has $[a]_D + 59 \cdot 6^\circ$, the specific rotation of bornylamine being $[a]_D + 57 \cdot 1^\circ$. It appears, therefore, that the symmetrical replacement of both atoms of aminic hydrogen, involving comparatively slight change in the disposition of nitrogen with regard to asymmetric carbon, produces a correspondingly small increase in rotatory power, and it became of interest to ascertain whether bornylamine derivatives of the type $C_{10}H_{17}$ ·N:CHR would exhibit the optical properties of dialkylbornylamines, or whether a

disturbing influence would be exerted by the presence of an unsaturated linking.

Attempts were made to obtain substances of the nature indicated by condensing bornylamine with acetaldehyde and propaldehyde, but although combination occurs very readily in each case, the products are ill-defined oils which boil over a range of several degrees. Attention was therefore devoted to the condensation products of bornylamine with various aromatic aldehydes, and in the following table a comparison is made between the optical activity of each derivative and that of the original base:

	$[a]_{D}$ in benzene.	[M] _D in benzene.	[a] _b in alcohol.	[M] _p in alcohol.
Bornylamine	+ 57·1°	+87:3	+46.2°	+70.7
Benzylidenebornylamine	27 · 4	66.0	62.6	150.8
Orthonitrobenzylidenebornylamine.	41.6	118.9	8-6	24.5
Paranitrobenzylidenebornylamine Orthohydroxylbenzylidenebornyl-	23.0	65.8	51·5	147.3
amine Parahydroxylbenzylidenebornyl-	_	_	112:3	288-6
amine	_	_	107-1	275-2

It is evident from these results that no relation, similar to that connecting bornylamine with its dialkyl compounds, exists between the primary base and its aromatic aldehyde derivatives. That the difference between the types $C_{10}H_{17}\cdot N$:CHR and $C_{10}H_{17}\cdot NX_2$ must be ascribed to the presence of an ethylenic linking, appears from the following comparison of benzylidene compounds with the corresponding benzyl derivatives:

	[a], in benzene.	Difference.	[a] _p in alcohol.	Difference.
BenzylbornylamineBenzylidenebornylamine	+84·1° 27·4	- 56·7°	+75·7° 62·6	-13:1*
Orthonitrobenzylbornylamine Orthonitrobenzylidenebornylamine.	74·0 41·6	-32:4	61 -2 8 -6	- 52 6
Paranitrobenzylbornylamine	77 ·9 23 ·0	- 54 9	66·6 51·5	-15-1

According to these data, a noticeable diminution in rotatory power attends the transition from a benzyl derivative of this series to the corresponding benzylidene compound, and it seems highly probable that an ethylenic linking in the neighbourhood of an asymmetric carbon

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atom is capable of exerting a perceptible influence on the optical activity to which the asymmetry of that carbon atom gives rise (compare Haller and Muller, Compt. rend., 1899, 128, 1370). It is also noteworthy that the difference in rotatory power between paranitrobenzylbornylamine and paranitrobenzylidenebornylamine approaches closely to the corresponding difference between benzylbornylamine and benzylidenebornylamine, but is quite unlike that between the ortho-derivatives. This is a fresh instance of closer resemblance to the parent compound on the part of a para- than of an ortho-derivative (compare this vol., p. 939), and another case is furnished by the nitrobenzylidenebornylamines, of which the paracompound has a molecular rotation almost identical with that of benzylidenebornylamine, but differing most widely from the molecular rotation of the ortho-derivative.

There is one point of chemical interest in connection with benzylidenebornylamine of which brief mention has been already made (loc. cit.). When this base is heated with methylic iodide in a sealed tube, a crystalline additive compound is produced, which, under the influence of water, is resolved into benzaldehyde and methylbornylamine hydriodide according to the equation

 $C_{10}H_{17} \cdot N(CH_8)I \cdot CH \cdot C_6H_5 + H_9O = C_6H_6 \cdot CHO + C_{10}H_{17} \cdot NH \cdot CH_8$, HI.

The usual difficulty of preparing in quantity the monomethyl derivative of a primary base has been overcome by this means in the case of bornylamine, but the reaction does not seem to be general, and is probably confined to saturated bases. Benzylidene-β-naphthylamine. for instance, when heated with methylic iodide at 120° and then extracted with ethylic acetate, yields trimethylnaphthylammonium iodide; benzylidenephenylhydrazone gives rise to dimethylaniline and a malachite-green.

The behaviour of benzylidenebornylamine towards methylic iodide is very similar to that of benzylideneaniline towards acetic chloride, the additive compound from which yields acetanilide, benzaldehyde, and hydrochloric acid on hydrolysis; the description of this change (Garzarolli-Thurnlackh, Ber., 1899, 32, 2277) appeared simultaneously with the brief notice of benzylidenebornylamine methiodide (this vol., p. 936).

EXPERIMENTAL.

Benzylidenebornylamine, C₁₀H₁₇·N:CH·C₆H₅.

The compound obtained by the union of bornylamine with benzaldehyde was described by Griepenkerl as a colourless oil (Annalen, 1892, 269, 353). It has been shown, however, that the method at that time employed for preparing bornylamine gives rise to a mixture

of two isomerides (Forster, Trans., 1898, 73, 386); if these are separated from one another before treatment with benzaldehyde, the benzylidene derivative of the idextrorotatory base is found to be crystalline.

25 grams of bornylamine were treated with 17 grams of benzaldehyde, which dissolved the base and became warm, yielding a turbid, oily liquid; this was heated on the water-bath during some minutes, and afterwards cooled with ice, when it rapidly solidified to a hard, crystalline cake. The product was then fused beneath a small quantity of hot alcohol, and rapidly cooled, the colourless crystals thus obtained being collected with the aid of a pump and finally recrystallised from alcohol, which deposits benzylidenebornylamine in rosettes of long, lustrous needles. It melts at 58—59°.

0.1709 gave 0.5279 CO_2 and 0.1509 H_2O . C = 84.24; H = 9.81. 0.3038 , 16.2 c.c. moist nitrogen at 17° and 771 mm. N = 6.28. $C_{17}H_{23}N$ requires C = 84.64; H = 9.54; N = 5.81 per cent.

A solution containing 0.5013 gram in 25 c.c. of benzene at 20° gave $a_D + 1^\circ 6'$ in a 2-dcm. tube, whence the specific rotatory power $[a]_D + 27\cdot4^\circ$; 0.5127 gram dissolved in 25 c.c. of absolute alcohol at 19°, gave $a_D + 2^\circ 34'$, corresponding to $[a]_D + 62\cdot6^\circ$.

Benzylidenebornylamine does not combine with hydrogen cyanide. It forms a clear solution in cold, concentrated hydrochloric acid, and is precipitated from the liquid by alkalis, but if the acid solution is boiled during a few minutes, benzaldehyde is regenerated, and then alkalis precipitate bornylamine.

The platinochloride separates almost immediately when platinic chloride, dissolved in alcohol, is added to an alcoholic solution of the base; it forms lustrous, transparent, six-sided plates, and decomposes at 245°.

0.2029 gave 0.0444 Pt. Pt = 21.88. $(C_{17}H_{23}N)_2, H_2PtCl_6$ requires Pt = 21.80 per cent.

The methiodide was prepared by heating 4.3 grams of benzylidene-bornylamine with 15 grams of methylic iodide in a sealed tube at 120—150° during 2 hours. The contents of the tube remain liquid at 30°, below which temperature crystals slowly separate; the product is treated with ether, filtered, and washed with ether, 5.7 grams of the salt being obtained in this way. The methiodide crystallises in pale yellow plates, and melts at about 215°, forming a deep red liquid which evolves gas.

0.1698 gave 0.1049 AgI. I = 33.36. $C_{17}H_{23}N, CH_8I$ requires I = 33.16 per cent.

The methiodide frequently melts indefinitely, and contains proportions of iodine which differ considerably from those required by theory; a specimen decomposing at about 200° contained 30.5 per cent. of iodine, the proportion of which was increased by recrystallisation from methylic iodide. If the methiodide is recrystallised from solvents containing water, dissociation occurs, and methylbornylamine hydriodide is produced. For instance, a solution containing 0.2527 gram in 25 c.c. of alcohol gave the specific rotatory power $[a]_D + 21.8^\circ$; in the case of complete dissociation, $[a]_D + 22.3^\circ$.

In order to prepare methylbornylamine from benzylidenebornylamine, the methiodide is heated with 5 parts by weight of ethylic acetate in a reflux apparatus during half an hour; the solvent is for the greater part removed by distillation, and the crystalline residue, when filtered from the solution of benzaldehyde in ethylic acetate, is recrystallised from water. Methylbornylamine hydriodide obtained in this manner melts at 251°, and has $[\alpha]_D + 26.6°$ in a 1 per cent. solution in absolute alcohol.

Action of Phenylhydrazine on Benzylidenebornylamine.—Benzylidenebornylamine was mixed with 1 mol. of phenylhydrazine, forming a stiff paste which rapidly became hard; when heated on the waterbath, the mixture did not melt, as would have been the case if no combination had occurred, but became red, and smelled of bornylamine. After digesting with cold, dilute hydrochloric acid, the undissolved portion was collected and identified with benzylidenephenylhydrazine, whilst the filtrate, rendered alkaline with caustic soda, yielded bornylamine.

Orthonitrobenzylidenebornylamine, C10H17·N:CH·C8H4·NO2.

When equal quantities of bornylamine and orthonitrobenzaldehyde are intimately mixed, a viscous, turbid oil is produced, which rapidly becomes crystalline. Orthonitrobenzylidenebornylamine separates from alcohol in lustrous, colourless plates and melts at 71°; it becomes bright yellow, and finally dark brown, on exposure to light.

0.1891 gave 0.4946 CO₂ and 0.1274 H₂O. C = 71.33; H = 7.49. $C_{17}H_{22}O_2N_2$ requires C = 71.32; H = 7.68 per cent.

A solution containing 0.5010 gram in 25 c.c. of benzene at 23° gave $a_D + 1^\circ$ 40' in a 2-dcm. tube, whence $[a]_D + 41.6^\circ$; 0.5080 gram dissolved in 25 c.c. of absolute alcohol at 23° gave $a_D + 21'$ in a 2-dcm. tube, corresponding to $[a]_D + 8.6^\circ$.

Paranitrobenzylidenebornylamine, C₁₀H₁₇·N:CH·C₆H₄·NO₂.

Six grams of bornylamine were mixed with the same weight of paranitrobenzaldehyde, and heated at 80° until a homogeneous product was obtained; when cold, the turbid, viscous liquid rapidly solidified on being stirred with a glass rod. Paranitrobenzylidenebornylamine separates from light petroleum in large, yellow, transparent crystals; it melts at 75°.

0.1244 gave 0.3247 CO₂ and 0.0876 H_2O . C = 71.18; H = 7.82. 0.2266 , 20.5 c.c. moist nitrogen at 25° and 769 mm. N = 10.21. $C_{17}H_{99}O_2N_2$ requires C = 71.32; H = 7.68; N = 9.79 per cent.

A solution containing 0.4069 gram in 25 c.c. of benzene at 15° gave $a_D + 45'$ in a 2-dcm. tube, whence $[a]_D + 23.0^\circ$; 0.4487 gram, dissolved in 25 c.c. of absolute alcohol at 23°, gave $a_D + 1^\circ$ 51' in a 2-dcm. tube, corresponding to $[a]_D + 51.5^\circ$.

Orthohydroxybenzylidenebornylamine, $C_{10}H_{17}$ ·N: $CH\cdot C_6H_4\cdot OH$.

When bornylamine (4 parts) is dissolved in salicylaldehyde (3 parts), considerable rise of temperature takes place, and a turbid, bright yellow oil is produced, which solidifies after several days. Orthohydroxybenzylidenebornylamine crystallises from light petroleum in bright yellow, transparent prisms and melts at 62°; it dissolves very readily in alcohol, light petroleum, and ethylic acetate.

0.2369 gave 0.6894 CO_2 and 0.1913 H_2O . C = 79.36; H = 8.97. $C_{17}H_{28}ON$ requires C = 79.37; H = 8.95 per cent.

A solution containing 0.4877 gram in 25 c.c. of absolute alcohol at 23°, gave $a_D + 4^\circ$ 23' in a 2-dcm. tube, whence $[a]_D + 112.3^\circ$.

Parahydroxybenzylidenebornylamine, C₁₀H₁₇·N:CH·C₆H₄·OH.

Bornylamine was intimately mixed with parahydroxybenzaldehyde in molecular proportion, the stiff paste thus produced being heated on the water-bath until it solidified. The parahydroxy-compound, which is colourless, crystallises from ethylic acetate in lustrous, square, transparent plates, and melts at 162°; it dissolves in hot benzene, but is very sparingly soluble in the cold medium.

0.1510 gave 0.4376 CO₂ and 0.1222 H₂O. C = 79.04; H = 8.99. $C_{17}H_{23}NO$ requires C = 79.37; H = 8.95 per cent.

A solution containing 0.5054 gram in 25 c.c. of absolute alcohol at 15° gave $a_{\rm D} + 4^{\circ}$ 20' in a 2-dcm. tube, whence $[a]_{\rm D} + 107.1^{\circ}$.

The anisylidene and cuminylidene derivatives are oils, and were not further investigated.

ROYAL COLLEGE OF SCIENCE, LONDON, SOUTH KENSINGTON, S.W.

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CXIX.—The Interaction of Sodium Hydroxide and Benzaldehyde.

By Charles Alexander Kohn, Ph.D., B.Sc., and William Trantom, Ph.D., B.Sc.

THE reaction between benzaldehyde and caustic alkalis, as employed for the preparation of benzylic alcohol, is represented by the well known equation:

$$2C_6H_5 \cdot CHO + NaOH = C_6H_5 \cdot CH_2OH + C_6H_5 \cdot COONa.$$

Caustic potash is generally employed in the preparation in preference to caustic soda, according to the method detailed by R. Meyer (*Ber.*, 1881, 14, 2394).

In the course of some experiments on condensation products of benzaldehyde in presence of small quantities of alkali, it was observed that an immediate flocculent and bulky precipitate is produced on the addition of a concentrated caustic soda solution to benzaldehyde. The sudden nature of the change, which is accompanied by a distinct rise in temperature, indicated the possibility of an intermediate stage in the reaction, and a series of experiments were accordingly carried out with the view of isolating, or otherwise proving the presence of an intermediate compound. The results have not led to the isolation of such a compound, but we have obtained satisfactory indirect evidence of the formation of an intermediate ortho-derivative, analogous to that described by Claisen (*Ber.*, 1887, 20, 646) as the product of the action of sodium methoxide on benzaldehyde.

When sodium methoxide reacts with benzaldehyde, white, bulky solid is formed which, when decomposed by water, yields sodium benzoate and benzylic alcohol, just as benzaldehyde does with caustic alkali. If, however, the solid product is first treated with glacial acetic acid and then with water, benzylic benzoate, benzylic alcohol, and methylic benzoate, with only a trace of benzoic acid, are obtained. This

result is attributed by Claisen to the formation and decomposition of an intermediate ortho-compound,

Such a compound would be immediately decomposed by water into sodium benzoate, benzylic alcohol, and methylic alcohol, whilst of itself it can break down either into benzylic benzoate and sodium methoxide, or into sodium benzylate and methylic benzoate. It is on the formation of an analogous benzylic compound that Claisen has based his excellent method for the preparation of benzylic benzoate (loc. cit., p. 649).

The results of the following experiments prove that, in the absence of water, or in the presence of an excess of benzaldehyde, benzylic benzoate is a product of the action of sodium hydroxide on benzaldehyde. formation may be due to the action of benzylic alcohol on sodium benzoate in presence of the glacial acetic acid used for decomposing the first product of the reaction, or to benzylic benzoate itself being the initial product of the reaction, or finally to the decomposition of an intermediate ortho-compound. To test the first possibility, sodium benzoate and benzylic alcohol were heated together in glacial acetic acid solution for 4 hours, but the whole of the original products were recovered without the formation of any benzylic benzoate. When benzylic benzoate itself is treated with caustic soda under the conditions employed in the action of the alkali on benzaldehyde with subsequent decomposition by water, the hydrolysis of the ester is incomplete, whilst benzaldehyde is completely converted into the alcohol and acid by the theoretical quantity of caustic soda at the ordinary temperature. Further, if the ester be the original product, it should be present, irrespective of whether the presence of an excess of aldehyde or the absence of water is a condition of the reaction, and this is not the case. The formation of an intermediate ortho-compound is the remaining possibility to explain the production of the ester, and the experimental evidence is wholly in favour of this view.

From this standpoint, the action of caustic soda on benzaldehyde takes the following form:

$$C_6H_5 \cdot CHO + NaOH = C_6H_5 \cdot CONa \\ O \cdot CH_6 \cdot C_8H_6$$

In presence of water, decomposition into benzylic alcohol and sodium benzoate, the ordinary products of the reaction, will occur:

In the absence of water, two decompositions are possible:

I.
$$C_6H_5 \cdot C = OH_5 \cdot COONa + C_6H_5 \cdot CH_2OH$$
.
 $O \cdot CH_2 \cdot C_6H_5$ = $C_6H_5 \cdot COO \cdot CH_2 \cdot C_6H_5 + NaOH$.
II. $C_6H_5 \cdot C = OH_5 \cdot COO \cdot CH_2 \cdot C_6H_5 + NaOH$.

The first decomposition takes place far more readily than the second; it is favoured by an excess of alkali, whilst an excess of aldehyde favours the latter: facts which corroborate this view of the reaction.

The experimental results show that Nef's suppositions (Annalen, 1897, 298, 301) in regard to the course of the reaction between benzaldehyde and caustic alkalis are unnecessary, and they bring the change into line with the analogous reactions studied by Claisen.

There are two ways in which the aldehyde groups of 2 molecules of benzaldehyde can give rise to the formation of condensation products. One of these is the well known benzoin condensation, the other should lead to the formation of benzylic benzoate, thus:

(i)
$$-C \triangleleft_{O}^{H} + -C \triangleleft_{O}^{H} = -CH(OH)-CO-$$

Benzoin condensation.

(ii) $-C \triangleleft_{O}^{H} + -C \triangleleft_{O}^{H} = -CO-O-CH_{2}-$

Benzylic benzoate condensation.

The latter change, however, as shown in the following experiments, takes place only as the result of the formation of an intermediate compound, and it is probable that the production of an additive compound also precedes the benzoin condensation. This point is under investigation, especially with respect to the use of dry materials in the reaction.

In a recent paper by Haller on compounds of camphor with aldehydes (Compt. rend., 1899, 128, 1270), the formation of piperonylic piperonate by the action of piperonaldehyde on sodium camphor is attributed to the presence of sodium borneol in the mixture; since, however, caustic soda is liberated in the formation of the condensation product, piperonylidenecamphor, which is the chief product of the reaction, it appears extremely probable that the formation of piperonylic piperonate, which is accompanied by some piperonylic alcohol, is really due to the action of the liberated alkali on the piperonaldehyde. If so, the formation of the ester is an interesting confirmation of the above view of the interaction of aldehydes and caustic alkali. In a previous paper (Compt. rend., 1891, 118, 22) on the same subject, camphylic salts of the acids corresponding with the aldehydes employed are described as secondary products of the reaction and their formation is accounted for on the lines of the reactions studied by Claisen.

There is one other possible course for the reaction between benzaldehyde and caustic soda, namely, that the two molecules of aldehyde condense directly to an unsaturated glycol: $\begin{array}{c} C_6H_5 \cdot C \cdot OH \\ C_6H_5 \cdot C \cdot OH \end{array}$. This represents a tautomeric form of benzoin, the dibenzoyl and diacetyl derivatives of which are known, but no indication of the formation of such a compound or of its derivatives was obtained. It could yield benzoic acid and benzylic alcohol very simply, thus:—

but the formation of benzylic benzoate from it would not depend on the absence of water, or the presence of an excess of aldehyde.

EXPERIMENTAL.

Action of Caustic Soda on Benzaldehyde in Presence of Water.

A number of experiments were first tried in which an aqueous solution of sodium hydroxide was added to benzaldehyde in the proportion of one molecule of the former to two of the latter. precipitate that is formed immediately, increases in bulk rapidly on standing, and the reaction may be completed either by heating the mixture on the water-bath for 3 hours, or by allowing it to stand, with repeated shaking, for a day. To 53 grams of benzaldehyde, 10 grams of caustic soda dissolved in 15 grams of water were added. The final product consisted of a hard cake, which was dissolved in 75 c.c. of warm glacial acetic acid, and the solution diluted with water, made alkaline, and extracted with ether; the oil obtained by evaporation of the ethereal solution was then fractionated. The alkaline solution was acidified and the precipitated benzoic acid collected. Under these conditions, benzylic alcohol and sodium benzoate proved to be the sole products; it is a matter of indifference, therefore, whether water or glacial acetic acid is used in the decomposition of the final product of the reaction.

The yield of benzylic alcohol under these conditions is extremely good, 90 per cent. of the theoretical yield being obtained, and by increasing the proportion of sodium hydroxide to 20 grams, a theoretical yield (98 per cent.) resulted. This is consequently a better, as well as a cheaper, method for the preparation of benzylic alcohol than that usually employed.

Action of Solid Caustic Soda on Benzaldehyde.

10 grams of caustic sods were ground to a fine powder under benzene, washed into a flask with benzene, and a solution of 53 grams

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of benzaldehyde in 100 c.c. of benzene added. During the addition, the mixture was well shaken; after a short time, the whole set to a hard mass. This was heated in a reflux apparatus on the water-bath for 2 hours, the mass being broken up and shaken several times during the heating. The solid residue was ground up in one case with ether, and in another with benzene, the extracts filtered, and the residues fractionated after distilling off the solvent, but in both cases only benzylic alcohol together with some unchanged benzaldehyde was left, the yield of the former amounting to 76 per cent. of the theoretical.

In these experiments, no special care had been taken to render the materials anhydrous, but the necessity of this condition became obvious when the structure of a possible intermediate product was taken into account. As shown on p. 1157, a molecular proportion of water is regenerated in the action; this, therefore, will suffice to effect the complete breaking down of the compound into benzylic alcohol and sodium benzoate. In the subsequent experiments, the caustic soda was first ground up under benzene to prevent undue absorption of moisture during the grinding, the greater part of the benzene drained off, and the rest removed by drying in an exsiccator. The final drying was effected in a vacuum over phosphoric oxide repeatedly renewed. Only small quantities of caustic soda, spread over a large surface, were dried at a time. The benzene employed as solvent was distilled over sulphuric acid and phosphoric oxide successively. periments were made with materials thus prepared. In both cases, the mixture became solid very soon, athough in one (No. II) the aldehyde was added very gradually, and the temperature kept down by means of ice previous to the heating on the water-bath. The product of the reaction was first dissolved in glacial acetic acid, the solution diluted with water, and then extracted with ether after the The following are the details of these two exaddition of alkali. periments, 200 c.c. of benzene being used in each:

Benzaldehyde (grams).	Caustic soda (grams).	Time of standing.	Time of heating.	Unchanged benz- aldehyde (grams).	Sodium benzoate and benzylic alcohol formed (grams).	Benzylic benzoate formed (grams).	Proportional decomposition into benzylic benzoate and caustic sods.
122	23	48 hrs.	1½ hrs.	20	91	10	11·5
106	20	12 ,,	2 ,,	5	84	8	10·0

The presence of unchanged benzaldehyde in both cases is due to the difficulty of effecting a complete reaction in the solid mass, although it was broken up and thoroughly mixed several times during each experiment.

Claisen obtained from 10 to 40 grams of benzylic benzoate from 106 grams of benzaldehyde by the action of sodium methoxide. It therefore appears that the methylic ether of the ortho-compound breaks up somewhat less readily than the simpler derivative into the alcohol and acid (methylic ester). The benzylic ether is still more stable in this respect.

The benzylic benzoate boiled at 280—320°, and was therefore accompanied by some benzylic alcohol. Carefully fractionated, it yielded a product boiling at 310—320°, which gave the following results on analysis:

0.2089 gave 0.6074 CO₂ and 0.1132 H₂O. C = 79.30; H = 6.02. $C_{14}H_{12}O_2$ requires C = 79.25; H = 5.66 per cent.

Pure benzylic benzoate was found to boil at 316.8°, as determined by an Anschütz thermometer with its stem immersed in the vapour (Claisen gives 323—324°). That the product was benzylic benzoate was confirmed by hydrolysis with alcoholic potash, when benzylic alcohol and potassium benzoate were obtained.

Action of Caustic Soda on an Excess of Benzaldehyde.

In the above experiments, the theoretical quantity of caustic soda required by the equation was employed. In order to obtain a condition more favourable to the decomposition of the ortho-compound into benzylic benzoate and caustic soda, an excess of benzaldehyde was used with which the liberated alkali might react until the decomposition was complete. The results and conditions of this series of experiments are tabulated below. The formation of benzylic benzoate when an aqueous solution of caustic soda was used, is a most satisfactory proof of the formation of the intermediate ortho-compound. With dry solid caustic soda, it was found extremely difficult to complete the reaction, since the mass cakes together and the excess of aldehyde thus largely escapes further action. This is doubtless the reason why the extent of the decomposition as well as the quantity of ester found as the product of the decomposition is not greater. The alkali was not always added at once, being sometimes introduced in portions at intervals of several hours. In all cases, the mixtures were heated on the water-bath for the times stated, and the products of decomposition worked up as described above.

No. of experiment.	Benzaldehyde (grams).	Caustic soda, per- centage of theoreti- cal quantity.	Conditions of experiment,	Time of heating (hours).	Sodium benzoate and benzylic alcohol formed (grams).	Benzylic benzoate formed (grams).	Percentage decomposition into benzylic benzoate and caustic soda.
I. II. IV. V.	106 106 53 53 59	75 25 20 75 82	Aqueous solution Solid under benzene	11 31 20 10 29	81 21 7 17 18	4.5 5 1.5 4.5 5.5	6 22 20 24 27

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In experiments I and II, the total decomposition corresponds approximately to the maximum for the quantity of caustic soda employed, but in experiments III, IV, and V, carried out with dry materials and solid caustic soda, only from 30—50 per cent. of the total decomposition has been effected.

Action of Caustic Soda on Benzylic Benzoate.

If the supposition is correct that an intermediate ortho-compound is formed in the action of caustic soda on benzaldehyde, the same product should result when benzylic benzoate is treated with caustic soda. 26 grams of benzylic benzoate, dissolved in 100 c.c. of benzene, were treated with 5 grams of dry solid caustic soda. No appreciable action took place until the mixture was heated on the water-bath, when, after 6 hours, the whole became nearly solid. The product was dissolved in water and examined, with the result that altogether 20 grams of sodium benzoate and benzylic alcohol were isolated, 10 grams of the ester remaining unchanged, thus proving that benzylic benzoate is not the initial product of the action of caustic soda on benzaldehyde.

Action of Sodium Benzyloxide on Benzaldehyde.

4.6 grams of sodium were dissolved in 21.6 grams of benzylic alcohol in 125 c.c. of benzene, and 43.2 grams of benzaldehyde were added gradually. After shaking, the mixture was heated on the water-bath for 16 hours, the solid residue dissolved in water, extracted with ether, and the residue from the ethereal solution fractionated. The benzoic acid was separated from the alkaline solution by the addition of hydrochloric acid. The following products were obtained:

Unchanged aldehyde	nil.
Benzylic alcohol	18 grams.
Benzoic acid	8.5
Benzylic benzoate	29 ,,

In this case, therefore, despite the direct addition of water, decomposition into the ester proceeds to the extent of 54 per cent., and that into benzylic alcohol and benzoic acid only to the extent of 46 per cent. of the theoretical; the formation of these products, however, is a satisfactory confirmation of the correctness of Claisen's view. Also the relative stability of the methyl and benzyl ethers of the ortho-compound, as regards their decomposition into esters, is quite in accord with the influence of these substituting groups.

The decomposition of this benzyl ether by water into benzylic alcohol and sodium benzoate is represented by the equation:

The foregoing results lead naturally to the study of the influence of water in several reactions involving the use of alkalis, such as the two decompositions of ethylic acetoacetate and allied changes; also to the complex action of alkalis upon aliphatic aldehydes. These subjects, as also the action of alkalis on other aromatic aldehydes, are now under investigation.

University College, Liverpool.

CXX.—The Ultra-violet Absorption Spectrum of Proteids in Relation to Tyrosine.

By A. WYNTER BLYTH.

THE apparatus employed in the investigation of the ultra-violet absorption spectrum of proteids consists of a large quartz prism made of two halves of right and left hand rotation respectively.

A double quartz slit is used, as it possesses the advantage that two spectra are taken one above the other, one with a wide, the other with a narrow slit, so that when it is necessary to use a slit wide enough to blur the lines, the narrower slit will give the metallic lines sharply defined, and thus enable the position of any absorption bands to be measured.

The source of light is a powerful spark produced by a large coil charged either from storage batteries or from the main, the coil is provided with a Wehnelt's break, and one Leyden jar is used as a condenser. The optical train is quartz, and the image is thrown by a lens of 12 inches focal length on to a photographic film placed at a

proper angle. The tube bearing the slit is passed through a hole in the door of a dark room in which the instrument is placed.

The poles used have been various: cadmium, cadmium and nickel, nickel and iron, nickel and copper. To obtain an interpolation curve, poles made of an alloy of mercury, zinc, cadmium, and tin were employed, a photograph being taken of the metal under examination with the centre of the slit blotted out by a screen; on the same film,

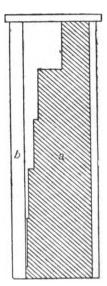
the spectrum of the alloy was next taken, using a second screen so arranged that the spectrum would occupy the blank space left by the first. Since all the wave-lengths of cadmium, mercury, zinc, and tin in the ultra-violet are well known, the spectrum of the alloy with its very numerous lines acted as a natural scale.

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The liquids under examination have been examined in ordinary cells closed by quartz plates, but as the cleansing of these cells was found to be troublesome and tedious, the author devised a special absorption cell * which promises to furnish important aid in researches of this kind. The cell consists of a block of quartz (a) cut into successive steps, the faces of the steps and the back are perfectly parallel and highly polished, the cell is completed by a quartz plate in front (b), the sides being of ground glass, a metal frame provided with screws acting on small plates of metal, securely presses the plates of glass and quartz



together, the top is closed with a glass plate, which is kept in place by a screw. The steps in the present cell are cut so as to give successive thicknesses of 1, 2, 4, 8, and 16 mm. The cell is supported on a stand capable of moving by rack-work. The photographic slide is similarly moved by rack-work. Five photographs on the same film can thus be taken in less than 5 minutes. If other thicknesses are required, they can be obtained in the ordinary way.

Animal and Vegetable Albumin.

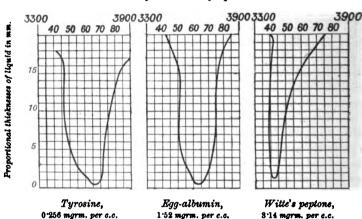
According to Soret, diluted egg-albumin gives a single absorption band of wave-lengths 2880—2650. Hartley (Trans., 1887, 51, 59) confirms this statement, giving the band in wave-lengths as 2948—2572.

The author has investigated the absorption spectrum of egg-albumin, serum-albumin, animal casein, and vegetable casein, as well as of Witte's peptone, and also finds a single band.

The cell was constructed by Mr. Hilger, of Stanhope Street.

The egg-albumin, purified by frequent precipitation, was diluted and filtered through several hardened filter papers, and ultimately an almost limpid solution obtained. A fractional part of the solution was evaporated on a platinum dish until it ceased to lose weight, and the residue ignited and weighed; the solution was then diluted until it attained the strength desired. A similar process was adopted with both vegetable casein, legumin, and serum-albumin.

It was found that the absorption bands of these substances differed quantitatively rather than essentially in character. The following are the measurements obtained with solutions of egg-albumin and Witte's peptone, it being understood that, although wave-lengths in four



Scales of Oscillation frequencies.

figures are given, the wave-length is taken from a definite metallic line bordering the absorption band; in point of fact, the bands are never so definite, being diffuse at the edges.

Solution	q f	egg-albumin	in	water	(1	c.c.=1.52	milligram	q f
			al	bumin)	١.			

Thickness of film in mm.	Oscillation frequencies. 1/\lambda.	Absorption band.	Spectrum ends. A.
20	3439—3766	2980—2655	2415
15	3509—3784	2850—2643	2405
10	3509 3766	2850-2655	2385
5	8509—3766	2850—2655	2360
			l

Solution of Witte's peptone in water (1 c.c. = 3.14 milligrams of peptone).

Thickness of film in mm.	Oscillation frequencies. 1/\lambda.	Absorption band.	Spectrum ends. A.	
20	3478—8788	2875—2648	2260	
15	3478-3588	2875—2826	2260	
10	34783538	2875—2826	2258	
5	3478—3538	2875-2826	2256	

There are, however, quantitative differences between the different absorption spectra. Solutions containing equal amounts of nitrogen give absorption spectra of unequal length, Witte's peptone extending farthest into the ultra-violet, then come, in succession, legumin, eggalbumin, serum-albumin, and an alkaline solution of casein.

Each of these substances may be made to yield tyrosine by appropriate treatment.

Solution of tyrosine in water (1 c.c. = 0.256 milligram of tyrosine).

Thickness of film in mm.	Oscillation frequencies. 1/\lambda.	Absorption band.	Spectrum ends.
16 8 4 2 1	3470—3861 3471—3748 3581—3731	2882—2590 2880—2668 2792—2680	2405 2360 2305 2272 2272

Solution of tyrosine in water (1 c.c. = 0.126 milligram of tyrosine).

Thickness of film in mm.	Oscillation frequencies. 1/A.	Absorption band.	Spectrum ends. A.
16 10 8 5 4 2	8470—3784 8509—3571 8558—3676 8558—3676	2882—2648 2850—2680 2810—2720 2810—2750 Faint band	2877 2345 2335 2385 2315 2315 2305

The chief features of these absorption bands are indicated in the curves on p. 1164.

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It is thus seen that the absorption spectrum of tyrosine is practically identical with that of the proteids enumerated. The author has little doubt that the single absorption band given by the various vegetable and animal albumins is due to the fact that tyrosine enters into their structure.

Albumoses and Gelatin.

Schrötter (Monatsh., 1893, 14, 612) has described an albumose possessing very definite properties. Briefly, it is prepared by acting on an acidified solution of Witte's peptone with zinc dust, filtering, evaporating to dryness in a vacuum at the ordinary temperature, taking up with methylic alcohol, in which it is soluble, and reprecipitating with ether. The albumose may be obtained pure by precipitating several times. It contains $C=51\cdot0$, $N=16\cdot8$, $H=6\cdot4$, $S=1\cdot1$ per cent., and gives all the ordinary reactions of an albumin.

This substance was dissolved in water, diluted, and a series of absorption spectra taken from extinction of most of the ultra-violet to almost perfect transparency, but no selective absorption could be discovered.

A pathogenic toxalbumin from diphtheria, submitted to the author by Prof. Sidney Martin, gave the usual absorption band of albumin.

A toxalbumin from a case of ulcerative endocarditis, also strongly poisonous, and submitted by Prof. Martin, gave a continuous spectrum.

Gelatin from various sources also failed to show selective absorption.

It therefore seems to the author that proteids might be divided conveniently, from a chemical standpoint, into those which show the tyrosine absorption band and those in which the band is absent—a division which is correlated with a profound difference in molecular composition.

ANNUAL GENERAL MEETING,

MARCH 29th, 1899.

Professor DEWAR, F.R.S., President, in the Chair.

Dr. A. Voelcker and Mr. W. P. Bloxam were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's address.

The President, in beginning his address, said that the past two years had been marked by change in the ranks of the active officers of the Society. Last year, Professor Thomson, who had been an Honorary Secretary since March, 1883, resigned office. His services to the Society had been beyond praise, not only from the amount of work actually done, of forethought and care expended, but also from the personal influence which enabled him to discharge the often delicate duties of his office without wounding the susceptibilities of those with whom he had to deal. Dr. Wynne, who became Junior Secretary last year, had now resigned the post to take up the arduous duties of Editor of the Society's Journal. Dr. Thorpe, who had been honorary Treasurer since 1889, vacated the office that day, the eminent services which he has rendered, not only to Chemical Science, but to the Society, recommending him to the Council for the highest honour the Society had to bestow. Dr. Tilden, who had served the Society twice as Vice-President, would succeed him as Treasurer, and Dr. Scott had been nominated to succeed Dr. Wynne as Secretary. The names of these gentlemen were familiar to the Society as those of persons in every way qualified to discharge the duties of their respective offices.

The Treasurer, as he might still for some minutes call him, would no doubt render them an account of his stewardship, but the duty was incumbent upon him of expressing their deep sense of the debt of gratitude owed him by the Society. During 10 years of office, despite the magnificent undertakings of which Dr. Thorpe had been

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the mainstay, the investments of the Society had increased by one-half, and its income had risen from £4150 to £5286, while, largely owing to his vigilant care, the tendency to an increased expenditure had been kept down to normal proportions.

During his term of office he had had to provide the funds for some very considerable undertakings, chief amongst which were the alterations effected in the meeting room and the introduction of the electric light in 1892, the Society's Jubilee in 1891, and the drawing up of General Indexes to the Society's Journal and the Abstracts from 1873 to 1892. On the completion of this latter piece of work, which Dr. Thorpe would announce to the meeting, it seemed a fitting time to acknowledge the service which the publication of these volumes has rendered to every one interested in the science. They had been issued gratuitously to all Fellows who had received the Journal during the period they cover, provided that application was made for them before December, 1895.

Though the initiative in this issue had been taken by our illustrious colleague, the main burden of the preparation of the Index had fallen on a lady, Mrs. Dougal, who edited the two volumes with zeal, energy, and intelligence. He (the President) would wish to bear testimony to her self-sacrificing devotion to this task, which had occupied upwards of five years. It had proved to be one of uncommon and unexpected difficulty. The annual indexing was found to have been done in an irregular and unsystematic way in the past, and much of the work which was understood to be ready to her hand had to be done over again. She had. both directly and indirectly, done the Society a great service—directly, by the compilation which she had executed, and indirectly, by leaving an example of thoroughness and accuracy to her successors. He had also to tender their thanks to the ladies who assisted her, and to Miss Neale, who had taken her place for a short time. The thanks of the Society were also due to the Index Committee, and more especially to Dr. Forster Morley, whose unwearied assistance and experience did much to solve the problems which were daily met with in the progress of the work.

The yearly indexes to the Journals had of late shown a tendency to expansion. With a view to making them of more service, a staff of Indexers, having a special knowledge of the various departments they undertook, had been engaged.

During the past year the Society was privileged to offer to six of its Past-Presidents its congratulations, and those of the whole Scientific world, on the occasion of their completing fifty years' Fellowship of the Society. The Banquet at which they were entertained would long live in their memory. To quote the words of Friedel, "No finer phalanx of the Fathers of our Science exists in any country." - The

occasion was too recent for him to add anything to the sentiments then expressed. The event, however, was not without a melancholy side. As originally proposed, the foremost of this phalanx would have been their senior Past-President, the last surviving Founder of the Society. He would not speak here at length of the services Lord Playfair had rendered to Science, but fifty years' active work in the service of the Society required a more special mention. He became a Member of the Council in 1846, in 1850 he was elected a Vice-President, in 1857 he became President of the Society in succession to Professor Miller, and from 1859, for forty years, he remained Vice-President of the Society to which his experience and influence rendered signal service. His last appearance amongst them had been to propose him (Prof. Dewar) as President.

During the past two years, the Society had lost by death thirty-six of its Fellows. Lord Playfair was the last survivor of the seventy-seven original members of our Society. In Mr. J. W. Rodger, the Society lost one of the most promising of the younger men of science and a Member of its Council. Sir Thomas Dyke Acland had been a Fellow of the Society for over forty years, and though he had never taken an active part in the affairs of the Society, he had rendered great services to our Science in its connection with Agriculture. Sir Douglas Galton, whose recent loss they had to deplore, had been a Fellow of the Society for a quarter of a century. Mr. Newlands, whose "Law of octaves" has taken an imperishable place in the history of Science, was in his fortieth year of membership, and had also served the Society as a Member of Council. His portrait now occupied a place on their walls.

Mr. Groves, who had been connected with the Journal since 1878, first as Sub-Editor, and, in 1884, as Editor in succession to Mr. Watts, resigned office that day. Only those who have been connected with similar publications could measure the full extent of the Society's indebtedness to him, but they could all join the Council in expressing their deep sense of, and thanks for, the important services he had rendered to the Society during those twenty-one years. They could only express the hope that his work for the Society and for Science might be continued for many years to come.

Mr. Greenaway, who had for so many years occupied the important office of Sub-Editor, and worked so harmoniously with Mr. Groves, had elected to remain in that position. Dr. Wynne had succeeded Mr. Groves in the editorial chair and could be trusted to preserve that high level of excellence to which the Society's Journal had attained.

The number of papers read before the Society during the past two years was 274, of which 216 had since been published in full in the

Society's Transactions, the remaining papers being preliminary notices of a more or less temporary character.

The Meetings of the Society had been well attended, and the discussions fruitful of interest, but he could desire, in the best interests of the Society, that a larger proportion of the senior Members could find it possible to be present.

During the past two years considerable attention had been given by the Council to the question of a suggested revision of the Bye-Laws. It has been found that no important modification can be made in these without the grant of a new Charter, and it is thought that it is hardly worth while to introduce mere verbal changes which might, perhaps, make the meaning of the Bye-Laws more clear, but which, the Council is legally advised, are unnecessary in view of the established practice of the Society.

The next matter of importance which would engage the attention of the Society would probably be the issue of a new catalogue to the Society's Library. Originally founded in 1850, it then consisted of about 270 volumes of journals, 60 miscellaneous volumes, and 100 pamphlets. Its first catalogue was issued in 1851, a second catalogue was prepared by Mr. Watts and issued early in 1861, a third catalogue, now grown from 28 to 112 pages, was issued in 1869, and a fourth, of 138 pages, in 1874. In 1886, a new catalogue, arranged according to subject matter was drawn up by Mr. Warington from Mr. Watts' notes, and issued to the Society. It extends to 327 pages, and has an Author-index drawn up by Professor McLeod. The catalogue of 1886 contains entries of 5580 volumes of journals, 4223 books, and 1380 pamphlets. Since that time there have been added 3279 volumes of journals, 1361 books, and over 1600 pamphlets. The preparation and issue of this important work would necessarily involve some considerable time and expense to the Society.

One of the great needs of scientific workers is a ready means of acquainting themselves with the bearing and results of general scientific work. The publication of Abstracts of particular branches of science is, generally speaking, nearly complete, but there is great overlapping and waste of energy. The suggestion has been made that some change analogous to that recently carried out by the German Chemical Society should be made in the publication of our own Abstracts. All such proposals will have the fullest consideration of the Council, but it is clear that it would be unwise to ignore the grave consequences to the financial position of the Society which might result from any too precipitate change in the method of publication of the Abstracts. Without entering more fully on this question, he might

remark that there was still room for co-operation in this matter between the societies of this country.

They had been asked to co-operate with the American and the German Chemical Society in bringing about an International agreement upon the subject of Atomic Weights. The Council has appointed a Committee to consider the matter.

In the meantime, they had had the opportunity of co-operating in the movements designed to honour the memory of two illustrious chemists, Kekulé and Davy; the former by joining in the International Memorial to his memory, the latter by contributing, in conjunction with the Royal Institution and the Royal Society, to a fund designed to restore and preserve the memorial raised over his grave.

The remainder of the address was of a general and theoretical nature, dealing with recent advances in Chemical research, principally in connection with low temperatures.

The numerical strength of the Society was as follows:—

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Number o	f Fellows	s, March 31st, 1898	2140
,, ,,	"	since elected reinstated by Council	
Removed	on eacou	nt of non-payment of two	2275
		tions 15	
		12	
Deaths .	•••••		45
		s, March 31st, 1899	
Foreign M	lembers .		38

The names of those removed were:—E. S. Cameron; F. E. J. Cridland; F. W. S. Glenfield; E. Hawkins; L. W. Hawkins; A. J. Heath; W. Hesketh; H. Heywood; J. Hulme; F. Ibbotson; J. E. W. McFall; B. E. Smith; J. H. Starling; F. H. Wigham.

The following have withdrawn:—Bennett F. Davenport; Henry Winram Dickinson; Arnold Eiloart; K. S. Engineer; C. H. Reissman; A. G. Scorer; Bomanji Sorabji; Walter J. Sykes; William Gilchrist White; John Williams; W. M. Wilson; B. Winstone.

The following have died:—Sir T. J. Dyke Acland; W. R. Burnett; Michael Conroy; E. Rider Cook; Ramchandra Dutta; George Foord; Sir Douglas Galton; Jeremiah Head; J. G. Heywood; W. L. Hiepe; Charles Lowe; J. A. R. Newlands; Eugen Obach; Lord Playfair; Manning Prentice; H. W. Seely; Matthew Smith; Samuel Spencer.

The number of communications made to the Society during the year was 150.

One hundred and two papers were published in the Transactions for 1898, occupying 1047 pages, whereas in the preceding year 114 papers were published, occupying 1204 pages.

The following were the statistics relating to the Abstracts.

PART I.		
Organic Chemistry	Pages. 720	No. of Abstracts. 1187
PART II.		•
General and Physical Chemistry		344 .
Inorganic Chemistry		284
Mineralogical Chemistry		171
Physiological Chemistry		165
Chemistry of Vegetable Physiology and Agri-		
culture		159
Analytical Chemistry		516
	660	1639
Total in Parts I. and II	1380	2826

Seven hundred and twenty-seven volumes had been borrowed from the Library. The additions comprised 67 books, 285 volumes of periodicals, and 24 pamphlets.

Dr. Gladstone, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the Transactions.

Dr. Armstrong, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Dr. THORPE, F.R.S., the Treasurer, in giving an account of the Balance Sheet which he laid before the Society, duly audited, said:—

The receipts had been:—By admission fees and subscriptions, £4064; by sale of Journal and advertisements, £740 15s.; and by dividends on invested capital, £428 2s. 1d. The expenses had been:
—On account of the Journal, £3007 9s. 10d.; on account of the Proceedings, £287 6s. 10d.; on account of the General Index, £793 16s. 7d.; on account of the Library, £294 19s. 11d.; House expenses, £238 2s. 7d.; the total expenditure being £5415 6s. 8d. Grants amounting to £245 had been made to Fellows from the Research Fund during the year, and a sum of £1316 1s. had been invested in the purchase of £1400 India 2½ per cent. Stock.

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On laying down his office as Treasurer, to which he was elected in 1889, Dr Thorpe hoped that it might not be uninteresting to the Fellows if he gave a brief account of the financial progress of the Society during the ten years of his stewardship.

In 1889, the total assets of the Society, excluding the Research Fund, were £12,221; in 1899 they are £17,289.

The total assets of the Research Fund in 1889 were £5464; in 1899 they are £7618.

The aggregate total assets are now £24,907, as against £17,686 in 1889.

In 1889, the total receipts from Fellows were £3402; in 1899 they are £4064, or an increase of $19\frac{1}{2}$ per cent. The annual income from the sale of the Society's publications in 1889 amounted to £365; this year, including an outstanding item on account of advertisements, it is £760, or an increase of 108 per cent. This is due partly to the increased circulation of the Journal and partly to the increased price which can be obtained for it. The advertisements now bring in an income equivalent to about £2000 of funded property.

The total income of the Society from all sources in 1889 including the balances at the Bank was £5824; at the close of the present financial year it has amounted to £7180.

It will be seen, therefore, that whilst the receipts from the Fellows have increased by $19\frac{1}{3}$ per cent., the income of the Society has increased by 23·3 per cent., and the total assets, some of which may be counted upon to still further increase the annual income, have increased by 40·8 per cent.

But if it may be said of Societies, as of individuals, that their riches consist, not in the abundance of their possessions, but in the fewness of their wants, it is the experience of the Treasurer that the Chemical Society is by no means a rich corporation, for its wants advance, almost pari passu, with its possessions. His successor would find that, however ingenious he may be in securing money, the Society, with equal or with even greater ingenuity, will find a method of relieving him of it.

He regretted to find that he had—he hastened to add, by direction of the Council—signed cheques for a greater amount than any one of his predecessors. During the ten years he had been in office he had disbursed nearly £45,000 of the Society's money. In explanation of this, he might point out that the annual cost to the Society of its publications has steadily increased since 1889. In that year, the expenses connected with its publications came to £2565; this year, in spite of a considerable saving in the printer's bills, and in spite of the draconian methods of the Publication Com-

mittee, its publications, excluding the Collective Index, have cost £3370.

The expenses on account of the Library also steadily increase. In 1889, £196 was spent in books, periodicals, and binding; this year, which has been somewhat below the average of the preceding years, the amount has been £246.

The House expenses in 1889 came to £184; this year they are £238.

The total expenditure in 1889 was £3430; this year it has been £5415.

As regards these disbursements, he might be pardoned, perhaps, for pointing out that none of his predecessors had been called upon to spend so large an amount of the Society's money in what might be termed extraordinary expenditure. To begin with, his immediate predecessor handed him over—and it was his only legacy—certain applications for increase of salary on the part of the Editorial staff, and he was good enough to urge that he should deal with them liberally. The liberality has resulted in a difference of £1000 to the Society.

In 1891, the Society celebrated its Jubilee at a cost, notwithstanding the generous assistance of the Goldsmiths' Company, of about £450. In the following year, the alteration of the Meeting Room and the installation of the electric light was taken in hand, at a cost of £1490.

Shortly afterwards, the Society was called upon to provide for the declining years of an old and faithful servant. There was no circumstance connected with his official career as the Treasurer of the Society which he recalled with greater pleasure than its action in regard to Mr. Josiah Hall's pension.

In the early part of 1894, the Society determined to print a Collective Index of its publications from 1873 to 1892. This has proved to be even a more formidable undertaking than was expected. It has occupied nearly five years in execution, and has cost some £1740. It is now happily completed, and the Society may congratulate itself upon possessing an adequate key to the great store of chemical knowledge which it has accumulated during twenty years.

The revision of the Annual Indexes necessitated by this great work has shown the absolute need for their more systematic preparation. This has led to the establishment of a special staff of indexers, at an annual cost to the Society of upwards of £60.

Another item of expenditure which had arisen during his tenure of office is connected with the lectures which are given in memory of the deceased Foreign Members. The Society has now a collection of eight of these Memorial Lectures, all of which have been given gratuitously by

Fellows or friends on the invitation of the Council. Their publication has cost about £400. These lectures together constitute a most valuable record of contemporary chemical history, and it is hoped that, as the Council have directed, they may be issued in a separate volume, with the accompanying illustrations, before the end of the next financial year.

In their donations to funds connected with the illustrious names of Lavoisier, Davy, Stas, Kekulé, Cannizzaro, the Fellows have not been unmindful of their obligations to these great pioneers in chemical enquiry, nor have they been forgetful, as the gathering of last November showed, of their obligations to the pioneers in their own Society happily still amongst us.

The Account books of the Society show that what he had called the extraordinary expenditure which has been incurred during the last ten years is close upon £7000.

He thought, however, they would all feel that, in the enhanced position of their Society, in the greater comfort and convenience of their Meeting Room, in the improvement and increased value of their publications, they had had an abundant return for this expenditure. Although but for it he might have been able to add a few more thousand pounds to their capital account, he hoped the Fellows would not hold him responsible for this omission, but look with a lenient eye upon the financial transgressions of what he sometimes felt himself to have been—a too compliant purse-bearer.

Mr. DAVID HOWARD proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. F. J. M. Page, and carried.

The TREASURER, in responding, proposed a vote of thanks to the auditors.

Prof. Hodgkinson seconded the motion, which was unanimously adopted, and acknowledged by Prof. TILDEN on behalf of Dr. Horace Brown.

Dr. A. VOELCKER proposed a vote of thanks to the Officers and Council.

Mr. H. B. BAKER seconded the motion, which was unanimously adopted.

Prof. Dunstan, F.R.S., responded on behalf of the Council.

Prof. THOMSON, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Dr. MESSEL and carried.

Mr. GROVES, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected:—

President: T. E. Thorpe, Ph.D., D.Sc., LL.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir W. Crookes, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Sir E. Frankland, K.C.B., D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., LL.D., F.R.S.; J. H. Gladstone, Ph.D., D.Sc., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., V.P.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: C. E. Groves, F.R.S.; G. D. Liveing, M.A., D.Sc., F.R.S.; T. Purdie, Ph.D., F.R.S.; William Ramsay, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, M.D., D.Sc., F.R.S.; John M. Thomson, F.R.S.

Secretaries: Wyndham R. Dunstan, M.A., F.R.S.; A. Scott, M.A., D.Sc., F.R.S.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: William A. Tilden, D.Sc., F.R.S.

Other Members of Council: H. Brereton Baker, M.A.; E. J. Bevan; Frank Clowes, D.Sc.; H. J. H. Fenton, M.A.; W. Gowland; C. T. Heycock, M.A., F.R.S.; D. Howard; Rudolph Messel, Ph.D.; G. T. Moody, D.Sc.; H. Forster Morley, M.A., D.Sc.; Arthur Smithells, B.Sc.; James Walker, D.Sc.

THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND. FROM МАВСН 25тн, 1898, то МАВСН 25тн, 1899.

D.

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1898.		3	8. d.	£ s. d.	1898.		3	d.	3	•	જે.
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					Audited	Audited with vouchers) WILLIAM A. TILDEN (for Horace T. Brown),	or Ho	180	I. Br	(II)	4.
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THE TREASURER IN ACCOUNT WITH THE CHEMICAL

Dr.			đ.		_	
Balance at Bank, March 25th, 1898			iï	-	•	•
Transferred from Deposit Account Receipts by Life Compositions, Admission Fees and Subscriptions from March 25th, 1898, to March 25th, 1899;—		_	_	1,098 800	9	11
Life Compositions—5 at £30; 1 at £20; 2 at £15; 4 at £12; 2 at £10	268 528 2 2	0 0 0	0 0 0			
2 Subscriptions, 1895 , 22 1 Subscription , 1896 , 22 38 Subscriptions , 1897 , 22 472 , , 1898 , 42	4 2 76	0 0 0	0 0 0			
3 " " 1899 " 21	13	0	000	4,064	0	•
Jale of Journals , Proceedings ,, General Index: To the Public To Fellows Proceeds of Advertisements in Journal	655 11 22 7 48	18 10 10	00000			
Subscription from the Society of Chemical Industry to June, 1898	9	9	000	740	15	•
Repayment of Income Tax Year's Dividends on £8,730 Metropolitan Board of Works 3\(\frac{1}{2}\) per cent. Stock \$4,000 Consolon and North-Western Ballway Debenture Stock	227 1 106 30	6 9	0 8 0	14	1	9
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March 25th, 1899.		₹.	
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Metropolitan Board of Works 3; per cent. Stock	7.875	0	0
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London and North-Western Railway Debenture Stock	1,150	0	0
Cardiff Corporation 2 per cent Stock	1.075		0
India 24 per cent, Stock	1,820	0	0
•	17,289	_	_
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£7,180 17 8

£7,180 17 8

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SOCIETY, FROM MARCH 25TH, 1898, TO MARCH 25TH,	1899.				
			C	R.	
Expenses on Account of the Journal and Proceedings.		_	_		_
Salary of Editor	# s. 250 0	đ.	£	٤,	d.
Sub-Editor	200 0	Ŏ			
,, Sub-Editor's Assistant	10 10 8 11				
Abstractors' Fees	320 4	1			
Periodicals for Abstractors	10 4 1.631 3	0			
Printing Wrappers	84 14	0			
Distribution of Journal by Printers Society	830 1 10 9	8			
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Indexers' Fees (1898 Index)	62 14 1 10				
		_	8,007	9	10
Printing of Proceedings Distribution of Proceedings	208 12 78 14				
•			287	6	10
Publishers' Commission	68 19 6 11				
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Expenses on Account of the General Index,					
•					
Petty expenses	154 18 2 16				
Printing of Index, 1888-92 (Balance of Account)	335 19	7			
,, ,, ,, 1878–82	800 2	9	793	16	7
					•
Expenses on Account of the Library.					
Salary of Library Assistant Books and Periodicals	48 12	6			
Books and Periodicals Binding	186 8 60 2				
•	-		294		
Salary of Assistant Secretary			184 130		4
Wiscellaneous Printing			66	10	2
Printing List of Fellows Stationery			43 17		0
Legal Charges			48	4	Õ
Grants to Kekulé Memorial Fund. £25: to Davy Monument Fund. £20			7 45	7	0
Expenses on Account of Dinner to Past Presidents on November 11th, 1898;				·	Ī
Métropôle Account, \$46 10s.; Souvenir, \$29 0s. 6d.; Printing, \$33 17s. 1d.; Postage, \$14 8s. 5d.			123	16	0
					•
House Expenses.					
Providing Refreshments	18 1	3 4			
Lighting the Building(Gas, £20 17s, 11d.; Electric Light, £24 9s, 6d.)	45				
Heating the Building (Coals)	12 10 10 0				
Repairs Fire Insurance Premium (7 years)	26 1				
Petty House Expenses	80 (16 19				
Petty House Expenses	65 (
, ,, Uniform Annual Fee to Gate Porter	6 6				
Contribution to Fund for Widow of late Gate Porter	5 0				
Inhabited House Duty		, 8	238	2	7
Bank Charges on Country and Foreign Drafts Treasurer's Petty Cash Disbursements			0		4
,, Assistant			10		Ö
Postages, Assistant. Postages, 29 6s. 2d.; Postal Cards and Stamped Envelopes (Clay), \$18 15s.; Embossed Stamps, \$12 10s. Secretarial Postages.			40	,,	2
Secretarial Postages			1	5	ō
Purchase of £1,450 India 2½ per cent. Stock			1,316 449		0
,, in hands of Treasurer			119		3

Audited with vouchers and found correct.
25th March, 1899.

WILLIAM A. TILDEN (for Horack T. Brown).
R. J. FRISWELL.
ARTHUR W. CROSSLEY.

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INDEX OF AUTHORS' NAMES.

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Page. Col. Line. 1078 i 12* for "1889" read "1898."

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77 in Table in col. 3 omit (av = 0.49). 6 for 0.46 read 0.15. Line. Page. for "unprotected" read "protected."
,, "Schonbein" read "Schoenbein." 84 18 15 and 26 87 8* "nitrate" read "nitrite." 90 after "Holt and Sims" insert "(Trans., 1894, 65, 432.)" 95 20 for "nitrite" read "nitrate." 102 "nitrate" read "nitrite."
"solid" read "melted." 16 103 12 "must" read "might." 116 2 9* "S" read "80g." 118 "(HgN₂O₂)₂" read "2HgN₂O₂."
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"1399" read "182.99."
"8617" read "3612." 523 17* 621 6* 656 22 "tub" read "tube." 726 9 12 "66.9" read "6.69." 798 802 16 "barium carbonate" read "barium chloride,"

^{*} From bottom.

amine sulphate, 1.5 grams (=0.6 gram hydroxylamine) was dissolved along with 32 grams of sodium hydroxide in nearly 2 litres of water, and then a solution was run in, with stirring, of 7.5 grams of silver nitrate, which was a considerable excess, such as was used in the other experiments. The abundant, black precipitate was washed, exhausted with ce cold, dilute nitric acid, and the solution, neutralised as usual in my other experiments, gave no silver reaction for silver hyponitrite, and nothing more than a slow and very slight action on permanganic acid, which might be due to a trace of either nitrous or hyponitrous acid. It was easily seen that some nitrous acid was formed, by applying the iodide and starch test. Under the circumstances of my experiments. therefore, even when 7 per cent. of the nitrite had been reduced to hydroxylamine, there could have been no perceptible production of hyponitrite during the after oxidation of the hydroxylamine. metallic silver, washed out with dilute nitric acid ammonia, weighed 3.8 grams, the calculated quantity being 3.95 grams. nitrite detected in the mother liquor of the black precipitate had been formed in too small a quantity to materially affect the weight of the metallic silver.

Generally, sodium hydroxide was approximately estimated, after all the hyponitrite had been precipitated, by titration of the mother liquor with nitric acid, and of the silver oxide that had been precipitated along with the silver hyponitrite and the metallic silver. The amalgam used was of approximately known strength, ascertained, not by sampling, which is impracticable, but by uniformly preparing successive quantities, and sacrificing one to assay by dilute sulphuric acid and weighing the sodium as sulphate; after use in reducing nitrite, the sodium remaining in the mercury was sometimes determined in the same way. Nitrous oxide and nitrogen were not measured; their total nitrogen was found by difference, and their proportions had been sufficiently ascertained by de Wilde, as I have already said; but their relative abundance was estimated by a burning splint of wood, the reduction of the nitrite being always conducted in a loosely closed flask. range of this reaction was from that of a gas utterly extinguishing combustion to that of one which supported it most vividly; in any uniformly conducted experiment, the gases evolved towards the end behaved like those given off at first.

To ascertain the effect on its reduction by sodium of adding sodium

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^{*} It was proved many years ago that silver is insoluble in dilute nitric acid, the presence of nitrous acid being necessary to make it dissolve. But the contrary has been since asserted to be true where the silver is finely divided, as when precipitated. This error, as I must regard it, is due to precipitated silver when black or blackish containing suboxide, which gives it its colour: this is resolved by acids into oxide of silver, which dissolves, and metallic silver, which is left.

hydroxide to a concentrated solution of sodium nitrite (negative as this proved to be), two methods were adopted. In one, the amalgam was covered with a cold saturated solution of sodium hydroxide, which has no action on it, and then the concentrated solution of nitrite was slowly added; at first, the alkali greatly impedes the action of the amalgam on the nitrite, but when more of the solution of the latter is added, the action goes on faster and to the end, and gives the usual large proportion of hyponitrite with very little hydroxylamine. In the other, a concentrated solution of sodium nitrite and sodium hydroxide was treated with some of the amalgam; then more sodium nitrite was added, and then more amalgam. The result was the same as before. The object of working in this way was to obtain the effect, if any, of the most concentrated alkali from the first, without having to deal afterwards with a very large excess of alkali when the analysis had to be made.

I have also tried to ascertain the effect of diminishing the amount of alkali present. In acid reducing mixtures, nitrous acid becomes largely converted into hydroxylamine without production of hyponitrous acid, so that it seems probable that, could the alkali formed in the reduction of the nitrite by sodium be neutralised nearly as fast as it is produced, much hydroxylamine would be obtained and very little hyponitrite. The use of the ordinary acids for the purpose in such a way as to give conclusive evidence on the point does not seem to be practicable, whilst the great rapidity of the process of reduction makes the use of carbon dioxide (Aschan, Ber., 1891, 24, 1865) very unpromising. I have, therefore, tried the effect of adding ammonium acid carbonate along with the sodium nitrite, expecting the ammonia to be inactive. In one case, where I used the amalgam in large excess, much ammonium amalgam was formed, and, what was quite unexpected, neither hyponitrite nor hydroxylamine. In another experiment, in which the nitrite was kept in excess of the amalgam, the previous addition of the ammonium carbonate in excess was without any effect; the nitrite solution had to be used slightly dilute because of the carbonate, and gave, therefore, a little less hyponitrite (about 12.7 per cent. of the nitrite consumed) and a little more hydroxylamine (about 3 per cent.) than in the best way of working for hyponitrite. The presence of the ammonium carbonate was, therefore, without effect, the reaction between the nitrite and the sodium being already complete when the sodium oxide comes in contact with the water and ammonium carbonate.

I satisfied myself that a fairly concentrated solution of nitrite is uniformly reduced from the commencement to the end of the reaction if the temperature is kept tolerably constant, the method employed being to examine the gases in the way described, and the hyponitrite

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and hydroxylamine as follows. To a solution of nitrite, one-half only of the quantity of sodium amalgam required to reduce it was added, and it was then found to contain hyponitrite and hydroxylamine in the same relative proportion as if the nitrite had been fully reduced (with cooling), and in approximately half the quantities the nitrite would have yielded if the full amount of sodium amalgam had been added.

Sodium amalgam was proved to have little or no action on nitrous oxide by exposing the gas for a long time to its action. The amalgam was liquid, and, when shaken up with the moist nitrous oxide in a stoppered bottle, coated the sides of the bottle. With occasional vigorous shaking, the bottle was kept closed four days; when opened, it was found to contain the nitrous oxide little, if at all, deteriorated as a supporter of combustion. In another similar experiment, a saturated solution of sodium hydroxide was poured over the amalgam; in this case, the amalgam did not coat the sides of the bottle, but the solution served to keep the dissolved nitrous oxide in contact with the The bottle was often vigorously shaken, and was not opened until after four days. The nitrous oxide was almost or quite Holt and Sims have studied the oxidation of sodium and potassium by nitrous oxide, but only at much higher temperatures than those in these experiments, which were at 25-30°.

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petroleum. I, therefore, wrote to Prof. Aschan to ask him whether he had made any observations in this direction; he informed me, in reply, that he was chiefly interested in the "mechanism" of the reaction, and that he wished to continue the investigation from this point of view himself, but he very kindly expressed his willingness that I should compare the behaviour of the normal and isoparaffins towards chlorosulphonic acid, and that I should make use of the reagent as a means of purifying the paraffins.

As a preliminary experiment, I took equal small quantities of pure normal hexane and of isohexane, and added to each about its own volume of chlorosulphonic acid. The difference in the action was exceedingly marked; the isohexane became warm, and in a few moments bubbles of gaseous hydrogen chloride were rapidly evolved; the normal hexane, on the other hand, did not rise perceptibly in temperature, and it was only after some time that hydrogen chloride was given off. After standing all night, the isohexane had entirely disappeared, but about half the normal hexane was still left; the chlorosulphonic acid had changed to a dark, tarry oil, much blacker and thicker in the case of isohexane.

Again, pure normal octane from octylic iodide was far less rapidly attacked than normal octane separated from American petroleum by distillation.

In order to find whether normal paraffins from petroleum could be purified by means of chlorosulphonic acid, specimens of normal heptane and of normal octane freed from aromatic hydrocarbons were treated with about one-fifth of their volume of the acid and left in contact with it for two or three days, until the reaction had ceased. dark oil was in each case separated, and the remaining hydrocarbon was shaken repeatedly with strong sulphuric acid until, on dilution, the acid gave no turbidity with water. The hydrocarbon was washed with water, then shaken with caustic soda, and, lastly, with water again; it was dried with phosphorus pentoxide and distilled twice from an ordinary distillation bulb. The sp. gr. was then determined, and the treatment with chlorosulphonic acid repeated. There was not a sufficient quantity of either paraffin, and they were both too impure, to begin with, to allow of the treatment being continued until the sp. gr. had become constant, but the following table will show that the normal octane was obtained nearly pure and that considerable progress had been made in the purification of the normal heptane.

Normal Octans.

	8p. gr. 0°/4 e 0.71848	°. B. p. (760 mm.). 125.75°
Specimen from petro treatment with chloro	oleum before sulphonicacid } 0.7421	{ collected between } 125.2° and 127.0° }
After first treatment		125·2 —127·3°
" second " .	0·7224	125·7 —126·1°
" third " .	0.71956	125·75—125·95°

Normal Heptane.

Pure from Pinus sabiniana	Sp. gr. 0°/4°. 0.70048	B. p. (760 mm.). 98·45°
Specimen from petroleum before treatment with chlorosulphonicacid	0.7402	collected between } 98° and 102°
After first treatment	0.7319	99·1—100·3°
,, second ,,	0.7223	99·1— 99·6°

The normal heptane must have contained a little isoheptane and a large amount of methylhexamethylene, and the normal octane a little iso-octane and a larger quantity of, presumably, dimethylhexamethylene. The normal octane was less impure than the normal heptane, and there was more of it (about 50 grams before treatment with chlorosulphonic acid); it was, therefore, possible to carry the purification farther, and there can be little doubt that if the quantity had been larger the impurities might have been completely eliminated.

Miss Fortey has also found that impure hexamethylene from Galician petroleum, boiling at a somewhat lower temperature than the pure substance, and, therefore, containing methylpentamethylene and possibly some low boiling heptane, has both its sp. gr. and its boiling point raised by treatment with chlorosulphonic acid.

When chlorosulphonic acid is added to benzene, a violent action takes place, and torrents of hydrogen chloride are evolved.

The results obtained are sufficient to show that chlorosulphonic acid in the cold, like fuming nitric acid at a higher temperature, acts far less energetically on the normal paraffins than on the isoparaffins, the methyl derivatives of the polymethylenes or on benzene, also less energetically on the polymethylenes than on their methyl derivatives. Generally, chlorosulphonic acid acts more energetically on hydrocarbons that contain a :CH-group than on others.

There is, however, some action on the normal paraffins, and consequently there is considerable loss in the process of purification, just as there is with fuming nitric acid. In order to obtain the pure

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normal paraffins from petroleum, it would be best, before subjecting them to the action of chlorosulphonic acid, to separate them more completely from other hydrocarbons by fractional distillation than was done in the case of normal heptane or normal octane.

University College, Bristol. vacuum; prismatic needles of the copper salt gradually separate, and these, after draining on a porous plate, were analysed.

1.2784 lost 0.3010 H_0O at 160°. $H_0O = 23.51$.

0.2954 , 0.0780 CuO. Cu = 21.06.

 $Cu_8[OH(SO_8)_8]_2 + 12H_2O$ requires $H_2O = 23.71$; Cu = 20.74 per cent.

Ammonium Methanetrisulphonate, CH(NH₄SO₈)₃.—This was prepared by neutralising an aqueous solution of the pure acid with ammonia, and exposing the solution in a vacuum over sulphuric acid, when crystals of the salt separated.

0.2995 gave 0.0493 NH_8 . $NH_8 = 16.46$. $CH(NH_4SO_8)_8$ requires $NH_8 = 16.61$ per cent.

Ammonium methanetrisulphonate appears to crystallise in stumpy prisms or plates, probably belonging to the monosymmetric system. This research was carried out in the laboratories of the Owens College, Manchester, at the suggestion of Professor Perkin.

CRYSTALLOGRAPHICAL.

For the accompanying measurements of silver methanetrisulphonate, and description of the crystallographical character of the other salts of methanetrisulphonic acid, I am indebted to Mr. W. J. Pope.

Silver Methanetrisulphonats.—This crystallises in small, white, opalescent, iridiscent plates belonging to the orthorhombic system; the crystals are somewhat irregularly developed, and the faces in the zone [100:010] are deeply striated with lines parallel to the c axis. The extinction in $a\{100\}$ is parallel to the edge ap, and the acute bisectrix emerges normally to a(100); the optic axial plane is c(001), the optic axial angle is large, and the double refraction is negative in sign and weak.

Crystalline system.—Orthorhombic.

a:b:c:=2.9152:1:0.5422.

Forms present $a \{100\}$, $b \{010\}$, $p \{110\}$, $q \{011\}$ and $q' \{012\}$.

The following angular measurements were obtained.

Angle.	Number of measurements.	Limits.	Observed.	Calculated.
ap = 100:110 $bp = 010:110$ $pp = 110:110$ $pp = 110:110$ $bq = 010:011$ $qq = 011:011$ $qq' = 011:012$ $q'q' = 012:012$	17 39 24 20 32 24 11 16	18°22′— 19° 3′ 70 45 — 71 26 141 48 — 142 30 37 31 — 38 11 61 13 — 61 52 56 31 — 57 28 13 1 — 13 26 30 14 — 30 39	18°49′ 71 4 142 9 37 46 61 32 56 59 13 14 80 26	18°56′ 142 8 37 52 56 56 13 18 30 22

Barium Salt.—The crystals consist of minute, rhomboldal shaped plates, the acute angle being 76°; the extinction bisects the angles of the rhomb.

Sodium Salt.—The crystals consist of long, six-sided plates, in which the extinction is parallel to one pair of edges; the large face is perpendicular to the positive bisectrix of a large optic axial angle.

Potassium Salt.—The crystals consist of large, monosymmetric prisms, showing the forms {100}, {001}, {110}, and {111}. The optic axial plane is perpendicular to the plane of symmetry, and one optic axis emerges nearly normally through the face (110).

Forms observed.

C		{111}	•••••	{0001}
7.	•••••	{100}	•••••	{10 T 1}
8	•••••	{110}	•••••	{01 T2 }
p	•••••	{ T 10}	•••••	{2110}

The following angular measurements were obtained.

Angle.	Number of measure- ments.	Limits.	Mean.	Calcu- lated.	Miller.	Groth.
cr = 111:100	24	61° 0′— 61°11′	61° 6′	_	61° 9′	61°18′
cs = 111:011	15	42 5 - 42 18	42 10	42°10′	42 15	
rs = 100:011	17	103 7 103 24	108 16	108 16	•••	•••
$rs = \overline{1}00:011$	21	76 37 — 76 51	76 43	76 44	•••	•••
$pr = 10\overline{1} : 100$	20	40 35 40 53	40 43	40 42	40 39	
rs = 100:101	18	49 16 - 49 21	49 18	49 18	49 19	49 15
rr = 100:010	12	98 33 98 40	98 36	98 36 5	98 41	98 36
ss = 101:011	18	71 0 - 71 11	71 6	71 5.5	•••	
$pp = 10\overline{1} : 01\overline{1}$	10	59 62 60 6	60 0	60 0	•••	
rr = 100:010	9	81 5 - 81 26	81 23	81 23.5	•••	
$ps = \overline{1}10:011$	14	54 21 — 54 36	54 28	54 27	•••	

After melting on a microscope slide, the substance crystallises sluggishly, yielding a film which is full of cracks, and consists of large, individual flakes; these plates lie nearly parallel to the optic axis or perpendicular to $c\{111\}$, and, therefore, show negative double refraction. An optic axis is never seen emerging in the field; and the substance does not change in crystalline form if kept, photographs taken immediately after solidification being identical in appearance with pictures taken a month later.

CHEMICAL DEPARTMENT,

CITY AND GUILDS OF LONDON INSTITUTE,

CENTRAL TECHNICAL COLLEGE,

SOUTH KENSINGTON.

XLIV.—Contribution to the Characterisation of Racemic Compounds.

By A. LADENBURG.

The question whether an inactive substance is a mixture of the active components (d, l, mixture) or a racemic compound (r), has for a long time been open to discussion. I was certainly one of the first who occupied myself with this question, and during the past ten years

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have frequently taken the opportunity to discuss it (Annalen, 1888, 247, 66; Ber., 1894, 27, 3065; 1895, 28, 163 and 1991; and 1897, 30, 485). Many others have examined and studied thoroughly this problem, however, without being able to arrive at a complete solution.

Messrs. Kipping and Pope also have lately been studying this problem, and have come to the following conclusion.

"Only one method is at present of really practical use for characterising solid racemic compounds, that, namely, which is based on the determination of the crystalline forms of the optically active and externally compensated materials." This appears to me to be an attack on the views held by myself, and which I have already expressed as follows:—A mixture of enantiomorphic substances may be distinguished from a racemic compound by treating the substance in question, which must contain at least a small surplus of one or the other of the optically active modifications, with inactive substances. If this causes the substance to separate into fractions of different optical activity, it is a racemic compound.

The above-named investigators have tested my statement by experiment, but could not verify it; I, therefore, do not feel capable of maintaining it, but believe that the principle involved in it is correct, and has only been expressed in a misleading manner.

I give my previous statement, therefore, the following form:—To characterise an inactive substance, that is, whether it is a racemic compound, or a mixture of its active components, determine the solubility of the substance without and with the addition of a small quantity of one or the other of its optically active components at the same temperature and with the same solvent. If the solubilities are different, the substance in question is a racemic compound; if the same, it is an enantiomorphic mixture. (Mr. Pope's reply to Professor Ladenburg's statement will be found in the Proceedings, 1899, 15, 73.—[Editor.])

The correctness of this statement seems to me to be indisputable. I have verified it up till now by several examples which I shall continue to augment.†

1.—Racemic acid. Solubility in 100 parts of water at 18°.

* E. Fischer, Ber., 1894, 27, 1525 and 3224; 1896, 29, 2927; Wallach, Ann., 286, 140; Marchlewski, Ber., 1892, 25, 1561; 1895, 28, 1611; Winther, Ber., 1895, 28, 3000; I. Traube, Ber., 1896, 29, 1394; Kipping and Pope, Trans., Chem. Soc., 1897, 71, 989, and 1899, 75, 36; Landolt, Optisches Drehungsvermögen; Walden, Ber., 1896, 29, 1692; Van't Hoff, Ber., 1898, 31, 533; Küster, Ber., 1898, 31, 1847.

† I desire to expressly state that Van't Hoff ("Bildung und Spaltung von Doppelsalzen") employed the solubility determination with success in the investigation of similar problems (see also Küster).

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- I. and II. pure racemic acid III. Racemic acid with an addition of tartaric acid.
 - I. 16.590. II. 16.591. III. 18.95.
 - 2.—Pyrotartaric acid. Solubilities in 100 parts of water at 13°.
- I. and II. pure pyrotartaric acid. III. The same with an addition of d-pyrotartaric acid.
 - I. 34.83 II. 34.88. III. 38.27.
- 3.—Mixture of *d* and *l-sodium ammonium tartrats*. Solubilities in 100 parts of water at 12·3°.
 - I. Inactive mixture of equal quantities of the two salts.
- II. The same, with the addition of about 8 per cent. of d-sodium ammonium tartrate.
 - I. 43.53. II. 43.41.

By these experiments, it seems to be proved that racemic and pyrotartaric acids are racemic compounds, whilst d- and l-sodium ammonium tartrate remain uncombined in the solution at $12\cdot3^{\circ}$, which is quite in accord with previous experiments.

and -10.34° (o=5.51). The rotation of the methoxy-acid, like that of its homologue, is raised by alcohol. The following observations show that the rotation of calcium ethoxypropionate falls with rise of temperature, and that its behaviour therefore is not in accordance with the general rule, that rise of temperature and dilution produce similar effects.

$$p = 24.434$$
, $d 10^{\circ}/4^{\circ} = 1.0993$, $[a]_{D}^{10^{\circ}} = -37.75^{\circ}$
 $d 30^{\circ}/4^{\circ} = 1.0912$, $[a]_{D}^{20^{\circ}} = -35.48$.

To the distinctive points in the optical behaviour of lactic and the alkyloxypropionic acids previously indicated (Trans., 1898, 73, 877; 1899, 75, 160), we may now add the phenomena exhibited by the zinc and magnesium salts. A N/10 solution of zinc lactate, despite its comparatively slight electrolytic dissociation, gives a rotation which is not much short of the maximum rotation of the alkali salts; the rotations of the zinc alkyloxypropionates at similar concentration, though increasing rapidly, are still far short of the maximum. The molecular rotations of the lactates of the zinc group increase with molecular weight; the converse holds true for the alkyloxypropionates.

United College of St. Salvator and St. Leonard, University of St. Andrews. Our best thanks are due to Mr. Alexander Lauder, of the University College of North Wales, Bangor, for his assistance in the general work of the research, and especially for the great care he has taken in preparing the substances examined.

We are now engaged in a more comprehensive research on this subject, embracing the examination of the absorption spectra of derivatives of etheric succinosuccinates, phloroglucinol, and other substances which exhibit tautomeric phenomena.

The various expenses of this investigation were partly defrayed by a grant from the Government Grant Fund of the Royal Society.

ROYAL COLLEGE OF SCIENCE, DUBLIN. whether in the plant or by treatment with dehydrating agents. It is evident that the furfuraldehyde separated by distillation does not account for the total production of furfuran derivatives, since the hydroxy-derivative described in this paper would not accompany the furfuraldehyde, but would undergo decomposition during the reaction. It would seem, also, that the reaction of the pentoses themselves with phloroglucinol is due to hydroxyfurfuraldehyde formed in the process of condensation, and this also may in part account for the constant deficit of furfuraldehyde from the theoretical amount (64 per cent.) required by the equation

$$C_5H_{10}O_5 - 3H_2O = C_5H_4O_2$$
.

It is also well known that many oxy-derivatives of the hexoses, such as the glucosones and glycuronic acid, give relatively small yields of furfuraldehyde, although there is every reason to expect a much larger proportion of furfuran groups, and obviously there are many points in this special field of work which may be usefully revised in view of the results of the present investigations.

We are indebted to Mr. F. S. Young, M.A., and to Mr. J. S. Remington, for their kind assistance in the experimental work; we also have pleasure in stating that we are indebted to the Committee of the Royal Society for placing at our disposal a grant of money from the Government Research Fund.

liquid, an equally concentrated (2 per cent.) solution of paranitrobenzylbornylamine being practically colourless.

A solution containing 0.5082 gram in 25 c.c. of benzene at 15° gave $[\alpha]_D = 3^\circ 0.5'$ as the mean of ten readings in a 2 dcm. tube, whence $[\alpha]_D = +74.0^\circ$; a solution of 0.5068 gram in 25 c.c. of absolute alcohol at 22° gave $\alpha_D = 2^\circ 29'$, corresponding to $[\alpha]_D = +61.2^\circ$.

The hydrochloride forms highly lustrous, colourless scales, and has an intensely bitter taste; a 2 per cent. solution gave $\lceil a \rceil_p = +113 \cdot 2^\circ$.

The platinochlorids crystallises from alcohol containing hydrochloric acid in slender, highly lustrous, pale red needles.

0.1910 gave 0.0371 Pt. Pt = 19.42.

 $(C_{17}H_{24}N_2O_2)_2$ H_2 PtCl₆ requires Pt = 19.71 per cent.

The salt blackens and intumesces at 235°.

Paranitrobenzylbornylamine, C10H17·NH·CH2·C6H4·NO2.

The paranitrobenzyl derivative was prepared by the same method as that used for producing the ortho-compound, paranitrobenzylic chloride being substituted for the ortho-derivative. The dark brown residue obtained on evaporating the filtered alcoholic liquid was treated with dilute hydrochloric acid, the product being recrystallised twice from boiling water, and finally washed with ether on porous earthenware. On adding caustic soda to a boiling, aqueous solution of the salt, paranitrobenzylbornylamine was precipitated as a heavy, pale yellow, viscous oil which solidified on agitation in cold water; it was boiled with a quantity of alcohol insufficient to completely dissolve the fused base, then rapidly cooled, and recrystallised from hot alcohol, in which it is less readily soluble than the ortho-compound. It forms long, slender, lustrous needles which change into transparent, sulphuryellow prisms; the substance melts at 60—61°.

0.1583 gave 0.4129 CO₂ and 0.1245 H₂O. C = 71.13; H = 8.73. $C_{17}H_{24}N_2O_2$ requires C = 70.83; H = 8.33 per cent.

A solution containing 0.5082 gram in 25 c.c. of benzene at 15° gave $a_D = 3^{\circ} 10'$ as the mean of six readings in a 2 dcm. tube, whence $[a]_D = +77.9^{\circ}$; a solution of 0.5037 gram in 25 c.c. of absolute alcohol at 22° gave $a_D = 2^{\circ} 41'$, corresponding to $[a]_D = +66.6^{\circ}$.

The hydrochloride forms highly lustrous, colourless leaflets and does not melt below 250° ; a 2 per cent. solution in absolute alcohol gave $[a]_{0} = +20.3^{\circ}$.

The platinochloride crystallises from alcohol containing a large proportion of hydrochloric acid, in lustrous, red, transparent prisms.

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0.1829 gave 0.0356 Pt. Pt=19.46. (C₁₇H₂₄N₂O₂)₂,H₂PtCl₆ requires Pt=19.71 per cent.

The salt blackens and intumesces at 234°.

A subsequent communication will deal with the condensation products of bornylamine with aromatic aldehydes.

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was mixed with a long layer of lead chromate, with the following results:

```
0.2194 gave 0.3238 CO<sub>2</sub> and 0.0515 H<sub>2</sub>O. C=40.23; H=2.63. 0.3452 ,, 17.2 c.c. nitrogen at 13° and 756 mm. N=5.86. 0.1606 ,, 0.2906 AgCl. Cl=44.75. 0.516 liberated I=43.7 c.c. N/10 iodine. Cl, as :NCl, =14.88. C_8H_7NOCl_3 requires C=40.26; H=2.54; N=5.88; Cl=44.65; Cl, as :NCl, =15.02 per cent.
```

Two determinations of the molecular weight by Raoult's method were made, using 10 grams of benzene as solvent.

```
0.2010 lowered the freezing point 0.42°. M. wt. = 234.5.
0.6442 ,, ,, 1.295°. M. wt. = 243.7.
C<sub>e</sub>H<sub>7</sub>NOCl<sub>e</sub> requires a molecular weight of 238.45.
```

The behaviour of Witts's oil is identical in every respect with that of our crystalline 2:4-dichlorophenyl acetyl nitrogen chloride. When prepared by his method, it frequently solidifies with the greatest difficulty, owing to the presence of impurity, probably parachlorophenyl acetyl nitrogen chloride, which can only be removed by the treatment described above.

Phenyl Benzoyl Nitrogen Chloride, C6H5 NCl CO C6H5.

This substance is prepared by the general method from benzanilide and bleaching powder in the presence of potassium bicarbonate, but the reaction takes place less readily than with the formyl and acetyl compounds. It crystallises in colourless plates from a mixture of chloroform and light petroleum, and melts at 77°.

```
0.2014 gave 0.1228 AgCl. Cl = 15.08. C_{13}H_{10}NOCl requires Cl = 15.33 per cent.
```

On heating the melted chloride to 120—130°, benzoyl chloride is given off, whilst a portion is converted into parachlorobenzanilide. The latter change is brought about quantitatively if the nitrogen chloride is heated under water for some time.

Parachlorophenyl Benzoyl Nitrogen Chloride.

We have not succeeded in obtaining this substance pure, as parachlorobenzanilide is not attacked at the ordinary temperature by hypochlorous acid. At 70—80°, either in the presence of potassium bicarbonate or acetic acid, a reaction takes place, but at this temperature the chloride becomes partly converted into 2:4-dichlorobenzanilide, which in turn forms, with the hypochlorous acid, 2:4-dichloro-

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phenyl benzoyl nitrogen chloride. On extracting the product with chloroform, an oil is obtained which solidifies only with great difficulty. Analysis of the recrystallised product showed that it consisted of about 30 per cent. of parachlorophenyl benzoyl nitrogen chloride, together with 70 per cent. of 2:4-dichlorophenyl benzoyl nitrogen chloride.

2: 4-Dichlorophenyl Benzoyl Nitrogen Chloride, C. H. Cl. NCl·CO·C. H.

This compound, like the corresponding formyl and acetyl derivatives, can either be obtained directly from benzanilide or from 2:4-dichlorobenzanilide, by the action of bleaching powder in the presence of acetic acid at a temperature of from 80—90°. It resembles other members of the group in appearance and properties, and melts at 86°. On heating at 150—200°, benzoyl chloride is evolved and a tarry mass is left from which 2:4-dichlorobenzanilide can be isolated.

0.2096 gave 0.2992 AgCl. Cl = 35.3. $C_{18}H_8NOCl_8$ requires Cl = 35.44 per cent.

We have obtained similar compounds from many other substituted anilides, from secondary amines, and from other substances in which hydrogen is attached to nitrogen, and we desire to reserve the investigation of these compounds. We have also obtained substituted nitrogen bromides resembling the nitrogen chlorides very closely in properties.

CHEMICAL LABORATORY, St. Bartholomew's Hospital, E.C.

Solution of	Witte's peptone	in water	(1	c.c. = 3.14	milligrams
	of	peptone).			

Thickness of film in mm.	Oscillation frequencies. 1/\lambda.	Absorption band.	Spectrum ends.
20	3478—3783	2875—2643	2260
15	3478—3538	2876—2826	2260
10	3478—3538	2875—2826	2258
5	3478—3538	2875—2826	2256

There are, however, quantitative differences between the different absorption spectra. Solutions containing equal amounts of nitrogen give absorption spectra of unequal length, Witte's peptone extending farthest into the ultra-violet, then come, in succession, legumin, eggalbumin, serum-albumin, and an alkaline solution of casein.

Each of these substances may be made to yield tyrosine by appropriate treatment.

Solution of tyrosine in water (1 c.c. = 0.256 milligram of tyrosine)

Thickness of film in mm.	Oscillation frequencies. 1/\lambda.	Absorption band.	Spectrum ends, \(\lambda\).
16 8 4 2 1	84703861 34713748 35813731	2882—2590 2880—2668 2792—2680	2405 2360 2305 2272 2272

Solution of tyrosine in water (1 c.c. = 0.126 milligram of tyrosine).

Thickness of film in mm.	Oscillation frequencies. 1/A.	Absorption band.	Spectrum ends.
16 10 8 5 4 2	3470—3784 3509—3571 3558—3676 3558—3676	2882—2643 2850—2680 2810—2720 2810—2750 Faint band	2877 2845 2335 2335 2316 2316 2305

The chief features of these absorption bands are indicated in the curves on p. 1164,

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It is thus seen that the absorption spectrum of tyrosine is practical ridentical with that of the proteids enumerated. The author has litted doubt that the single absorption band given by the various vegetab and animal albumins is due to the fact that tyrosine enters into the structure.

Albumoses and Gelatin.

Schrötter (Monatch., 1893, 14, 612) has described an albumose possessing very definite properties. Briefly, it is prepared by acting or an acidified solution of Witte's peptone with zinc dust, filtering evaporating to dryness in a vacuum at the ordinary temperature, taking up with methylic alcohol, in which it is soluble, and reprecipitating with ether. The albumose may be obtained pure by precipitating several times. It contains C=51.0, N=16.8, H=6.4, S=1.1 per cent., and gives all the ordinary reactions of an albumin.

This substance was dissolved in water, diluted, and a series of absorption spectra taken from extinction of most of the ultra-violet to almost perfect transparency, but no selective absorption could be discovered.

A pathogenic toxalbumin from diphtheria, submitted to the author by Prof. Sidney Martin, gave the usual absorption band of albumin.

A toxalbumin from a case of ulcerative endocarditis, also strongly poisonous, and submitted by Prof. Martin, gave a continuous spectrum. Gelatin from various sources also failed to show selective absorption.

It therefore seems to the author that proteids might be divided conveniently, from a chemical standpoint, into those which show the tyrosine absorption band and those in which the band is absent—a division which is correlated with a profound difference in molecular composition.

The Report of the Annual General Meeting will be issued with the Supplementary Number containing the Index.

